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Tracking Hydroclimatic and Urbanization Impacts on Groundwater and Stream Water Evolution: A Tale of Two Carbonate Hydrologic Systems

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Tracking Hydroclimatic and Urbanization Impacts on Groundwater and Stream Water Evolution: A Tale of Two Carbonate Hydrologic Systems

by

Lakin Kathleen Beal

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Assessing the sensitivity of groundwater systems to hydroclimate variability is critical to sustainable management of the water resources of Guam, US territory. We assess spatial and temporal variability of isotopic and geochemical compositions of vadose and phreatic groundwater sampled from cave drip sites and groundwater wells, respectively, to better understand the vulnerability of the freshwater lens on Guam to variability in hydroclimate. We independently evaluate the existing conceptual model of the Northern Guam Lens Aquifer that is largely based on physical, as opposed to geochemical, observations. Sampling was conducted from 2008 to 2015, over which rainfall gradually increased. Major ion geochemistry and Sr isotope values of groundwater show varying influence from soil, limestone bedrock, and seawater. Geochemical modeling that explains spatial variability in groundwater Na^+ and Mg^{2+} concentrations and Sr/Ca and $^{87}Sr/^{86}Sr$ values indicates that groundwater compositions are dominantly controlled by mixing of freshwater with seawater and water-rock interaction. Differences between amount-weighted annual average precipitation $\delta^{18}O$ values and groundwater $\delta^{18}O$ values indicate a recharge bias toward the wet season, consistent with other tropical carbonate island aquifer settings. Intra- and inter-annual variations in Na^+ concentrations and $\delta^{18}O$ values in groundwater reflect sensitivity of recharge to seasonal variations in rainfall amount and changes in annual rainfall amounts. Our results indicate the influence of multiple modes of recharge on groundwater compositions and spatial variability in the sensitivity of groundwater to seawater mixing. This sensitivity of the freshwater lens points to the vulnerability of groundwater resources to changes in recharge associated with climate, land-use change, and increases in population.

2.0 Abstract

Quantifying urban development impacts on freshwater quality and quantity is critical, especially as growing populations concentrate in urban centers and with climate change projections of increased hydrologic extremes. We investigate geochemical processes through which municipal (supply and waste) water impacts stream and spring water compositions within the carbonate Bull Creek watershed (Austin, Texas), which exhibits a distinct geographic divide between urban development and rural land. $^{87}Sr/^{86}Sr$ and elemental variations are assessed for waters sampled from rural and urban sites to quantify relative influences of natural versus municipal water. Higher $^{87}Sr/^{86}Sr$ values for urban sites relative to rural sites can be accounted for by two models: (1) water leakage from municipal infrastructure and/or irrigation, or (2) ion exchange as precipitation infiltrates through soils with varying $^{87}Sr/^{86}Sr$. Irrigated soils have higher $^{87}Sr/^{86}Sr$ values than unirrigated soils, indicating that municipal water resets soil compositions, and that process (1) is a dominant driver of urban stream and spring water evolution. Fluid mixing models indicate that urban waters consist of 50% - 95% municipal water. Water-rock interaction modeling documents the geochemical evolution of infiltrating municipal water, whereby municipal water infiltrates as groundwater and undergoes diagnostic extents of water-rock interaction with the carbonate bedrock. These results are compared with regional phreatic and vadose groundwater compositions to infer local flow pathways and relative groundwater residences times of both municipal and rural water. This study advances our understanding of the significance of municipal water influences on urban stream water and soil compositions, and provides a geochemical modeling framework that quantifies the evolution of infiltrating municipal water within carbonate watersheds and aquifers.

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Thesis Overview

Sustainable management of freshwater resources is critical to ensure resilient communities through the 21st century. Challenges to conserving freshwater will become acute with the growing global population (U.N. Dept. of Economic and Social Affairs, 2017, U.N. Dept. of Economic and Social Affairs, 2014[II]), and with projections of an altered global hydrologic cycle as a result of climate change (IPCC, 2014 [II]). Surface and groundwater quality will become increasingly stressed as rapid urban development continues, especially in carbonate aquifers where high matrix porosity readily transmits contaminants (Wong et al., 2012 [II]; Smith et al., 2015 [II]). Understanding the modes in which water is transmitted (e.g., diffuse, conduit flow) and how water geochemically evolves within carbonate hydrologic systems is critical to understanding local to regional impacts to these freshwater resources. The thesis herein uses geochemical data and modeling techniques to draw links between hydrogeologic processes and freshwater resources within two carbonate hydrologic systems, specifically an aquifer (Chapter I) and a watershed (Chapter II). I assess both anthropogenic and hydroclimate impacts to freshwater resources among these two carbonate hydrologic systems, one published and one in review at scientific journals. Chapter I, "Isotopic and geochemical assessment of the sensitivity of groundwater resources of Guam, Mariana Islands, to intra- and inter-annual variations in hydroclimate" (Beal et al., 2019 [I]), applies geochemical and isotopic data (collected from 2008-2015) to further the scientific understanding of the carbonate island aquifer of Guam. These data are used to assess hydroclimatic and urban development impacts to fresh groundwater resources, specifically to independently assess the existing conceptual model of recharge and groundwater flow pathways through the carbonate aquifer. Isotopic and geochemical data for water samples from both groundwater wells and cave drip sites show that 1) variable modes of recharge occur throughout the aquifer (e.g., diffuse and conduit flow pathways), 2) recharge to the aquifer predominantly occurs in wet season months, and varies spatially, 3) the aquifer is sensitive to changes in inter-annual precipitation amount and intensity, and 4) the subsurface geology and presence/absence of underlying seawater controls the amount of seawater mixing in groundwater wells. This study provides independent constraints to an existing conceptual model (e.g., Gingerich, 2013[I]) by geochemically quantifying controls on recharge.

Chapter II, “Tracking the sources and processes of impacts on stream water evolution in a rapidly urbanizing watershed in Austin, TX” (Beal et al., in review[II]), applies geochemical data for spring and stream water, municipal (supply and waste) water, soil, and bedrock, in a semi-urbanized watershed (Bull Creek, Austin, TX; Senison, 2013[II]) to quantify the urban hydrologic cycle in a carbonate setting and to understand the impacts of urbanization on stream water quality. Specifically, I quantify the amount and varying flow pathways of infiltrating municipal water (via leakage and/or irrigation) that infiltrates as groundwater prior to stream discharge. Elemental and isotopic ($^{87}Sr/^{86}Sr$) endmember compositions are used to show that 1) irrigated municipal water resets natural soil composition over time, as evidenced by the differences in natural versus irrigated soil leachate $^{87}Sr/^{86}Sr$ values, 2) municipal water should be considered a significant source contributing to urban stream and spring water composition (up to 95% in this study), even when the watershed is semi-urbanized, and 3) water-rock interaction modeling can be used to identify the relative groundwater residences times and flow pathways of municipal water prior to stream discharge.

[I, II] Indicates the respective chapters in which the references appear

[*] Chapter I

Isotopic and geochemical assessment of the sensitivity of groundwater resources of Guam, Mariana Islands, to intra- and inter-annual variations in hydroclimate

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1.0 Abstract

Assessing the sensitivity of groundwater systems to hydroclimate variability is critical to sustainable management of the water resources of Guam, US territory. We assess spatial and temporal variability of isotopic and geochemical compositions of vadose and phreatic groundwater sampled from cave drip sites and groundwater wells, respectively, to better understand the vulnerability of the freshwater lens on Guam to variability in hydroclimate. We independently evaluate the existing conceptual model of the Northern Guam Lens Aquifer that is largely based on physical, as opposed to geochemical, observations. Sampling was conducted from 2008 to 2015, over which rainfall gradually increased. Major ion geochemistry and Sr isotope values of groundwater show varying influence from soil, limestone bedrock, and seawater. Geochemical modeling that explains spatial variability in groundwater Na^+ and Mg^{2+} concentrations and Sr/Ca and $^{87}Sr/^{86}Sr$ values indicates that groundwater compositions are dominantly controlled by mixing of freshwater with seawater and water-rock interaction. Differences between amount-weighted annual average precipitation $\delta^{18}O$ values and groundwater $\delta^{18}O$ values indicate a recharge bias toward the wet season, consistent with other tropical carbonate island aquifer settings. Intra- and inter-annual variations in Na^+ concentrations and $\delta^{18}O$ values in groundwater reflect sensitivity of recharge to seasonal variations in rainfall amount and changes in annual rainfall amounts. Our results indicate the influence of multiple modes of recharge on groundwater compositions and spatial variability in the sensitivity of groundwater to seawater mixing. This sensitivity of the freshwater lens points to the vulnerability of groundwater resources to changes in recharge associated with climate, land-use change, and increases in population.

1.1 Introduction

Sustainable management of fresh groundwater resources of carbonate island aquifers is critical to the health and well-being of current and future island communities and economies. The high matrix permeability of the bedrock in carbonate systems limits surface-water resources and typically makes groundwater the dominant source of potable water. Complex groundwater flow paths, dynamic interactions between the freshwater lens and underlying seawater, and changing land use and population growth can pose challenges to management of both the quantity and quality of groundwater (e.g., Chandrajith et al., 2016, Contractor and Jenson, 2000; Gingerich, 2003; Gingerich, 2013; Vacher and Mylroie, 2002, Rotzoll et al., 2013). Specifically, Guam's population is projected to increase from 180,000 in 2010 to 200,000 in 2020 (2010 US Census), and expansion of the US military (SEIS, 2018) could result in an additional increase in demand on the limited freshwater resources of the island (Gingerich, 2013). Links between the surface and subsurface can be strong in carbonate systems, making the freshwater lens sensitive to changes in climate that affect the hydrologic cycle (e.g., Wong et al., 2012; Jocson et al., 2002; Jones and Banner, 2003). That is, the future climate may have changes in evapotranspiration, the amount, timing, or intensity of precipitation, and/or the extent of runoff and recharge (Vorosmarty et al., 2000; Allen and Ingram, 2002), yet the effects on future recharge and thus water availability of the Northern Guam Lens Aquifer (NGLA) are not well known (Gingerich, 2013). Recent model projections indicate that Guam may experience a decrease in tropical cyclone activity (Kossin et al., 2016; Park et al., 2017; Widlansky et al., in press), and annual precipitation over the tropical Western North Pacific is projected to decrease as storm frequency and magnitude both decrease (Australian Bureau of Meteorology and CSIRO, 2011). Consequently, recharge to the NGLA would be expected to decline. Additionally, antecedent moisture conditions can significantly influence how water recharges the aquifer, especially in carbonate systems dominated by dual or triple porosities (e.g., Mahler et al., 2006; Wong et al., 2012). That is, carbonate systems can contain a combination of matrix porosity, fracture networks, and solution-enhanced fracture networks, shafts, and conduits. This range in porosity can simultaneously enable recharge through i) slow percolation through the bedrock matrix, ii) a relatively faster descent of a wetting front down a network of dissolution-widened fractures, and/or iii) rapid recharge via conduits and shafts that drain dolines.

The geology and hydrogeology of the NGLA have been studied for decades (e.g., Jenson et al., 2006; Jocson et al., 2002; Mink and Vacher, 1997; Mylroie et al., 2001; Mylroie and Jenson, 2000; Tracey et al., 1964; Ward, 1965) yielding a conceptual model of the groundwater system that describes a transition between the freshwater lens and seawater (Gingerich, 2013). Critical to the conceptual model is that the NGLA is a triple-porosity aquifer, with subsurface flow through matrix pore space between carbonate sediment grains, dissolution enhanced fracture networks, and conduits (Rotzoll et al., 2013). This porosity enables rapid recharge to the aquifer, and makes recharge sensitive to antecedent moisture conditions (Contractor and Jenson, 2000; Jocson et al., 2002, Schwarz et al., 2009).

Here we present results from an isotopic and geochemical study to provide insight into the sensitivity of the freshwater lens to climate variability, and provide independent constraints on the existing conceptual model of the groundwater system, which up to now has relied on physical, as opposed to geochemical, observations and constraints. We evaluate the major cation and isotopic ($\delta^{18}O$, δD, $^{87}Sr/^{86}Sr$) compositions of vadose cave dripwater and phreatic groundwater collected during 2008–2015 to delineate the sources and processes dictating groundwater compositions and characterize the response of groundwater to changes in climate.

Cave dripwater provides a unique window into Guam's thick vadose zone (60–180 m), which plays a critical role in transmitting recharge to the freshwater lens. There was a continual (monotonic) increase of rainfall from 2008 to 2015 (Supplemental Fig. S1.1) and the occurrence of El Niño and La Niña events enabling insight into the response of the groundwater system to inter-annual variations in rainfall amount (e.g., Fig. 1.4). Our results indicate the sensitivity of recharge to both intra- and inter-annual variations in hydrologic conditions as isotopic and geochemical compositions of the freshwater lens vary in response to seasonal and inter-annual changes in precipitation amount.

1.2 Hydrogeologic Setting

The NGLA (Fig. 1.1) is an eogenetic island karst aquifer, characterized by the development of porosity in young (Cenozoic) carbonates via meteoric diagenesis (Vacher and Mylroie, 2002). The aquifer has additionally been subject to post-depositional alteration and dissolution as a result of groundwater circulation. The fine-grained texture and poor sorting of the volcaniclastic basement rock that underlies the rocks of the NGLA results in much lower hydraulic conductivity than the overlying limestone bedrock (Fig. 1.2, Ward et al., 1965; Jocson et al., 2002). Miocene to Pleistocene marine limestone formations—the Barrigada and Mariana Limestones—occupy most of the surface of northern Guam (Tracey et al., 1964; Seymour and Schlanger, 1964). The Barrigada Limestone (> 140 m thick) forms the majority of the NGLA, and consists mostly of fine-grained foraminiferal grainstone (Tracey et al., 1964). The Mariana Limestone is composed of reef and lagoonal sediments, and occupies the coastal periphery and most (65%) of the surface outcrop of northern Guam (Tracey et al., 1964). It is generally coarser, more strongly cemented, and harder than the Barrigada Limestone. At the southwestern end of the limestone plateau, adjacent to the volcanic highland of southern Guam, the topmost unit is a wedge of argillaceous limestone containing fine-grained weathered volcanic sediment, and is mapped as the Hagåtña Argillaceous Member of the Mariana Limestone (Tracey et al., 1964).

Groundwater flow and storage within the NGLA is controlled by a triple-porosity system, including diffuse flow through matrix porosity (Fig. 1.2A and 1.2B), fracture flow through dissolution enhanced joints and fissures (Fig. 1.2C and 1.2D), and conduit flow in dissolution-enlarged fractures and vertical shafts draining dolines and along contacts between the limestone bedrock and volcanic basement (Jocson et al., 2002). Vacher and Mylroie (2002) showed that horizontal hydraulic conductivity in eogenetic island karst aquifers is a strong control on groundwater flow due to properties of the depositional environment and dissolution enhancement of matrix porosity at the water table. The regional hydraulic properties of the NGLA have been estimated from studies using field observations and numerical modeling to investigate the response of water levels to recharge (Jocson et al., 2002) and tidal-signal attenuation (Rotzoll et al., 2013). The Barrigada formation has estimated average matrix porosities of 0.13 and 0.21 above and below the water table, respectively, and groundwater flow largely occurs through secondary porosity ($K>12,000$ m/day), whereas the hydraulic conductivity of the Mariana Limestone is approximately 730 m/day with an average porosity of 0.13 (Rotzoll et al., 2013).

There are three groundwater zones within the NGLA: the basal, para-basal, and supra-basal zones (Gingerich, 2013) (Fig. 1.1). The freshwater lens in the basal groundwater zone is thin, occurs entirely within the limestone units, and is underlain by seawater. The freshwater lens in the para-basal zone is in contact with the underlying volcanic unit and, as a result, is less vulnerable to mixing with seawater. Groundwater in the supra-basal zone is underlain by volcanic basement and stands above mean sea level, and is, therefore, completely isolated from seawater.

Intra- and inter-annual variations in the thickness of the freshwater lens (e.g. storage) are influenced by the amount of recharge and withdrawal (Jocson et al., 2002; Gingerich, 2013). Guam has a tropical wet-dry climate with stable temperatures year-round and a mean annual rainfall of ~2.4 m, about 70% of which falls in the wet season from June to December (Supplemental Fig. S1.2). Recharge to the aquifer is estimated to be 50% of mean annual rainfall, but may vary locally from 40% to 60% (Johnson, 2012). Highest recharge rates occur in areas that receive runoff from urban storm drainage systems, whereas the lowest recharge rates occur in urban areas where stormwater runoff is routed to the ocean (Johnson, 2012). Additions to groundwater recharge occur in urban areas of northern Guam through irrigation, septic leachate, and water main pipe leakage (Johnson, 2012). Antecedent moisture conditions also play a role in transmission of recharge to the freshwater lens. Recharge may take several months to percolate to the lens under dry conditions, in contrast to rapid (hours to days) transmission of recharge under wet conditions or during high-intensity rain events (Contractor and Jenson, 2002; Jocson et al., 2002). Slower recharge rates under drier conditions likely reflects vertical propagation along a fine, fracture network, as opposed to direct recharge along discrete, solution-widened conduits that likely reflects high hydraulic conductivity estimated from regional-scale groundwater flow path studies. Furthermore, inter-annual variations in precipitation amount are sensitive to the El Niño - Southern Oscillation (ENSO), with wetter years corresponding to El Niño events (Guard et al., 1999; e.g. Fig. 1.4), and drier years, corresponding to La Niña events or the year following an El Niño event (Lander 1994).

1.3 Methods

Rainwater and groundwater from the vadose and phreatic zones were monitored over eight years (Partin et al. 2011; Noronha et al., 2016; Bautista et al., 2018). Rainfall was sampled every two weeks and cave dripwater was sampled every 4–6 weeks during 2008–2015, which spanned La Niña and El Niño conditions (Fig. 1.6, Supplemental Table S1.1). Groundwater from the NGLA was sampled quarterly from 10 wells from mid-2013 through 2015. The wells selected for this study are representative of the groundwater compositions for the three groundwater zones (Fig. 1.1), and span the six hydrologically connected groundwater basins that make up the NGLA (delineated by the Guam Environmental Protection Agency). Cave dripwater was collected at five sites (ST1, ST2, SMP, FTM, and TRN) within Jinapsan Cave that we hypothesize to represent water from dominantly diffuse (ST2 and SMP) and dominantly fracture flow paths (ST1, FTM, and TRN) based on their physical, isotopic, and geochemical properties (Fig. 1.7). This study draws on existing cave drip rate and cave dripwater $\delta^{18}O$ and cation (Ca concentrations and Mg/Ca and Sr/Ca values) data presented in Partin et al. (2011) and Noronha et al. (2016), which both focused on understanding how cave mineral deposits (speleothems) can be used to reconstruct past climate. This manuscript integrates existing cave dripwater data with previously unreported cave dripwater geochemical data (Na^+ and Mg^{2+} concentrations) and geochemical and isotopic data on phreatic groundwater compositions to investigate groundwater recharge processes. It should be noted that i) the vadose zone above the cave is a few meters thick, whereas the thickness of the vadose zone over the wells is well over 100 m, and ii) the cave is formed in Mariana Limestone, which is well-cemented compared to the well lithified to extremely friable Barrigada Limestone (Tracey et al., 1964) in which the 10 sampled wells were completed. Fractures are visible in the cave ceiling, and the more rapidly-dripping sites in the cave are associated with them (Bautista et al., 2018). Water samples were collected in pre-cleaned HDPE Nalgene bottles, and wells were sampled using plastic submersible bailers. The water samples were decanted into pre-cleaned glass vials with no head space for stable isotope ($\delta^{18}O$ and δD) analysis and acid-cleaned HDPE plastic vials for analysis of cation concentrations and Sr-isotope ($^{87}Sr/^{86}Sr$) compositions. Well-water samples were filtered using a pre-cleaned 0.45-micron syringe filtration in the field. Samples analyzed for cation concentrations and $^{87}Sr/^{86}Sr$ values were acidified with concentrated ultrapure HNO_3.

Cation concentrations were determined using Quadrupole Inductively Coupled Plasma (ICP)-Mass Spectrometry in the Department of Geoscience at the University of Texas at Austin (UT). Analytical uncertainty for Sr^{2+}, Na^{+}, Ca^{2+}, Mg^{2+} is $0.04x10^{-2}$, 0.02, 0.03, and 0.02 ppm, respectively, based on two times the standard error of replicate analyses of the internal standard. The median percent difference between replicate samples (n=99) for the Sr^{2+}, Na^{+}, Ca^{2+}, Mg^{2+} was 2.9%, 4.3%, 4.9%, and 5.6%, respectively (Supplemental Table S2). Detection limits for Sr^{2+}, Na^{+}, Ca^{2+}, Mg^{2+} (0.01, 1.47, 1.95, 0.29 ppb, respectively) are well below the elemental concentrations measured in collected samples (Supplemental Table S2). Waters were analyzed for stable isotope (δD and $\delta^{18}O$) compositions using a Thermo Scientific Delta V Isotope Ratio Mass Spectrometer (IRMS) equipped with a GasBench sample introduction system and Picarro L2130-i at UT. Uncertainty, based on two times the standard error of replicate analyses of internal standards, is ±8‰ for δD and ±0.2‰ for $\delta^{18}O$ for the IRMS and ±1‰ for δD and ±0.1‰ for $\delta^{18}O$ for the Picarro. Water isotopic measurements are reported in ‰ VSMOW. The mean difference between replicate analyses of δD (n=31) and $\delta^{18}O$ (n=62) was 5.8‰ and 0.3‰, respectively. Stable isotope data for rainfall were also retrieved from the Global Network of Isotopes in Precipitation (GNIP; IAEA/WMO, 2018). $^{87}Sr/^{86}Sr$ values of groundwater and leachates from surficial soil and saprolite samples were determined following the methods of Musgrove and Banner (2004) using a Thermo Triton Thermal Ionizing Mass Spectrometer (TIMS) at UT. The mean $^{87}Sr/^{86}Sr$ value for the standard NBS-987 was 0.71025 +/- 0.000016 (n=30). Blank values were negligible (7 pg of Sr^{2+}) with respect to sample size (200 ng). $^{87}Sr/^{86}Sr$ values for the limestone bedrock are estimated based on the secular seawater $^{87}Sr/^{86}Sr$ curve (Hodell et al., 1991, McArthur et al., 2006, Eidvin et al., 2014; $^{87}Sr/^{86}Sr$= 0.7088-0.7091), assuming that the limestone Sr isotope compositions have experienced negligible alteration by diagenesis. $^{87}Sr/^{86}Sr$ values for the volcanic bedrock values were obtained from Hickey-Varags and Reagan (1987; $^{87}Sr/^{86}Sr$= 0.7035-0.7038). Daily precipitation data were retrieved from the Guam Naval Air Station/Weather Forecast Office (NAS/WFO), the NOAA Weather Service Meteorological Observatory (WSMO), and Andersen Air Force Base (AAFB). AAFB and NAS/WFO are available from the National Climate Data Center, stations as “PGUA” and “PGUM”, respectively.

The evolution of dripwater Sr/Ca and $^{87}Sr/^{86}Sr$ values due to water-rock interaction is modeled following Banner and Hanson (1990). Here we consider water-rock interaction to include recrystallization of calcite or dolomite. Iterative mass-balance calculations simulate increments of water passing through a given volume of bedrock (measured in moles), assuming each increment of water comes to elemental and isotopic equilibrium with the bedrock. These equilibrium values are calculated using the partition coefficients of elemental systems (Sinclair et al., 2012). Initial dripwater Sr/Ca values were assigned based on the lowest value measured at each dripsite. That is, the lowest dripwater Sr/Ca values represent the least evolved waters via water-rock interaction, where higher Sr/Ca values (i.e. more evolved) will drive calcite minerals to precipitate. Initial dripwater $^{87}Sr/^{86}Sr$ values were assigned the median $^{87}Sr/^{86}Sr$ value from measurements of soil leachates (e.g., Banner et al., 1996; Musgrove and Banner, 2004; Wong et al., 2011; Wortham et al., 2017). Two sets of water-rock interaction trends were calculated using the highest and lowest bedrock $^{87}Sr/^{86}Sr$ values estimated for the limestone bedrock, which captures the range of possible dripwater values that could evolve by water-rock interaction. The varying isotopic composition throughout the Barrigada Limestone (> 140 m) is constrained to maximum (i.e. younger) and minimum (i.e. older) $^{87}Sr/^{86}Sr$ values (0.7091 and 0.7088, respectively) used in the model.

1.4 Results and Discussion

1.4.1 Delineating controls on phreatic groundwater compositions

Groundwater geochemical compositions are spatially variable, especially with respect to Mg^{2+} and Na^{+} concentrations (Fig. 1.3). Three end-member compositions were identified, i) low Na^{+} and Mg^{2+} concentrations (AG2A, and Y15, herein freshwater end member), ii) high Na^{+} and Mg^{2+} concentrations, herein group 2, and iii) low Na^{+} and high Mg^{2+} concentrations, herein group 3 (Fig. 1.3). One group of groundwater compositions is consistent with variable mixing (up to 1.5%) between the freshwater end member and seawater (Wells A10, F02, D14, and M18; referred to herein as Group 1). Another group of groundwater compositions deviates from the mixing line with elevated Mg^{2+} concentrations (Wells Y23, Y02, Y07, and M04; referred to herein as Group 2) (Fig. 1.3). Elevated Mg^{2+} concentrations in Group 2 might result from the interaction of infiltrating meteoric water with the carbonate bedrock. That is, water can interact with the bedrock via dissolution or recrystallization of the bedrock. Group 1 wells tend to be located to the north and/or west of Group 2 wells, and are within the basal zone (Fig. 1.1). Geochemistry of Group 1 groundwater indicates mixing between freshwater and seawater is a dominant control on groundwater compositions (Fig. 1.3), and is consistent with the description of the basal zone as where the freshwater lens is thin and underlain by seawater (Fig 1.1). Group 2 wells occur within the para-basal and supra-basal zones where the extent to which the freshwater lens is underlain by seawater, and hence susceptible to mixing, is limited.

Groundwater Na^+ concentrations exhibit limited temporal variability, with variations barely exceeding analytical uncertainty (±4.3%) (Fig. 1.4). At several wells, however, subtle variations are evident. For example, Wells A10 and Y15 have relatively low concentrations during the wet season (159 and 8.41 ppm, respectively) relative to the dry season (186 and 10.3 ppm, respectively). This indicates some dilution of Na^+ concentrations due to recharging rainwater reaching the freshwater lens. Additionally, several of the wells with low Na^+ concentrations (<20 mg/L; Wells AG2A, Y23, Y02, and M04) exhibit statistically significant decreasing trends in concentration over the study period (Supplemental Table S6), which is coincident with the continual increase of rainfall (Fig. 1.4 and Supplemental Fig. S1.1). Decreasing Na^+ concentrations at these sites indicate that the freshwater lens, in places, is sensitive to inter-annual variations in recharge. The occurrence of limited variations in Na^+ concentrations on intra- and inter-annual time scales indicates the sensitivity of parts of the aquifer system to changes in hydrologic conditions. The limited magnitude of variation in geochemical compositions, however, reflects the ability of water in storage to buffer water compositions to large changes in hydrologic conditions (e.g., transitions between wet to dry seasons). It is pertinent, however, that there were no storms during the study period of sufficient intensity to induce ponding in dissolution dolines or otherwise activate regional-scale conduit flow other than Typhoon Dolphin (May 2015) that only grazed the northern tip of the island.

Geochemical modeling of the evolution of the isotopic and geochemical compositions of groundwater can explain most groundwater Sr/Ca and $^{87}Sr/^{86}Sr$ values (Fig. 1.5). Infiltrating water initially acquires a $^{87}Sr/^{86}Sr$ value from the soil that tends to be higher than that of the underlying marine carbonate bedrock (0.7088-0.7091) (Fig. 1.5 inset). The $^{87}Sr/^{86}Sr$ value of infiltrating water gradually evolves via water-rock interaction to lower values that are more similar to that of the bedrock. In this process, water dissolves marine carbonates with higher Sr concentrations relative to the Sr concentrations in the calcite that is re-precipitated, thereby increasing the Sr/Ca value in the infiltrating water as the $^{87}Sr/^{86}Sr$ value is shifted toward that of the bedrock (e.g. water-rock interaction curves in Fig. 1.5; Banner et al., 1996; Musgrove and Banner, 2004; Wong et al., 2011; Wortham et al., 2017). Our model is constrained by measured values for soils and assumes values for the carbonate bedrock based on the age range of the Barrigada Limestone and the corresponding range of values from the reconstructed temporal variability in marine Sr-isotope values (Hodell et al., 1991, McArthur et al., 2006, Eidvin et al., 2014).

The large spread in possible bedrock values results in a large range of Sr/Ca and $^{87}Sr/^{86}Sr$ values to be accounted for by water-rock interaction, and, indeed, all but one of the groundwater compositions can be explained by this modeling effort (i.e., groundwater compositions in Fig. 1.5 fall between the two water-rock interaction curves). We note that the Sr/Ca and $^{87}Sr/^{86}Sr$ values from wells Y15, Y02, Y07, Y23 create a trend that parallels one of the water-rock interaction curves (Water-Rock Interaction II in Fig. 1.5), potentially reflecting the evolution of groundwater compositions via water-rock interaction with bedrock with similar $^{87}Sr/^{86}Sr$ values that are close to 0.7088. Importantly, these wells have Na^{+} and Mg^{2+} concentrations that indicate groundwater is not mixing with seawater at these locations in contrast to Group 1 wells (Fig.

1.3). Interestingly, Group 1 Sr/Ca and $^{87}Sr/^{86}Sr$ values do align with a mixing curve between the well interpreted as Freshwater (Y15) and seawater (Fig. 1.5). This supports the hypothesis that Group 1 groundwater compositions are dominantly influenced by seawater mixing with freshwater that has undergone water-rock interaction. Sr/Ca and $^{87}Sr/^{86}Sr$ values of M04 do not align with the rest of Group 2 compositions, and, instead, fall along the seawater-mixing curve in Fig. 1.5. This, however, is inconsistent with Na^{+} and Mg^{2+} concentrations that are not consistent with seawater mixing at this well (Fig. 1.3). M04 is spatially distinct from the other Group 2 wells, so the Sr/Ca and $^{87}Sr/^{86}Sr$ values that are distinct from other Group 2 wells might reflect water-rock interaction with bedrock of a different $^{87}Sr/^{86}Sr$ value.

1.4.2 A view of recharge from the vadose zone

Cave dripwater Mg^{2+} and Na^{+} concentrations are distinct relative to those of groundwater. Na^{+} concentrations of dripwater are elevated relative to those of Group 2, but Na^{+} and Mg^{2+} concentrations do not align with the freshwater-seawater mixing curve as do those of Group 1 well waters (Fig. 1.3). The inability of the freshwater-seawater mixing curve to account for the dripwater indicates that cave dripwater compositions are likely not strongly influenced by sea spray despite the proximity of the cave to the ocean. Both the Barrigada and Mariana Limestone Formations are high energy, reef-type settings in which deposition of evaporates was limited (Tracey et al., 1964), making the bedrock an unlikely source of Na^{+}. Variations, however, in cave dripwater Mg^{2+} and Na^{+} concentrations can be accounted for by evapo-concentration of freshwater (Freshwater Evaporation line in Fig. 1.3). Cave dripwater δD and $\delta^{18}O$ values fall on the Global Meteoric Water Line (GMWL), however, suggesting negligible influence of evaporation on the water isotopic compositions (Supplemental Fig. S1.3). Combined, these results indicate that water reaching the cave has undergone little evaporation, although the water infiltrating the cave is likely carrying salts precipitated from freshwater that previously evaporated. That is, rainfall that does not recharge the cave likely evaporates in the soil, epikarst, or shallow vadose zone, leaving behind salts that are later flushed into the cave during recharge intervals.

Seasonal variability in Na^+ concentrations is evident at two of the dripsites dominantly supplied by fracture flow (ST1 and FTM) (Fig. 1.4). Lower concentrations follow the wet season at these two sites, indicating the dilution of Na^+ concentrations of water stored in the vadose zone by infiltrating meteoric water, which is consistent with seasonal increases in drip rate. The presence of seasonal variability at some sites and absence at the other cave drip sites highlights the presence of distinct recharge pathways – diffuse pathways that drain the more homogenous and geochemically invariant water in storage in the vadose zone (Fig. 1.2A and 1.2B) (e.g. Moerman et al., 2014) and flow along dissolution enhanced fracture networks (Fig. 1.2C and 1.2D) that can by-pass much of the water stored in the vadose zone. Dripwater Na^+ concentrations exhibit a statistically significant decreasing trend over the entire eight years of monitoring at all of the drip sites (Supplemental Table S6 and Fig. 1.4). This consistent trend of decreasing Na^+ concentrations over the study period is consistent with i) increasingly higher drip rates during subsequent dry seasons over the study period at all the drip sites reflecting increased storage in the vadose zone (Fig. 1.4), and ii) increasing precipitation amounts over the study period (Fig. S1.1) driving dilution of Na^+ concentrations of water stored in the vadose zone by infiltrating meteoric water (Figs 4 and 6).

$\delta^{18}O_{precip}$ values exhibit prominent seasonal variability, with lower values during wetter months (Supplemental Fig. S1.2). Temporal variability in $\delta^{18}O_{precip}$ is greater than that for cave dripwater and groundwater (Fig. 1.6), likely reflecting homogenization of $\delta^{18}O_{precip}$ variability due to mixing in the vadose and phreatic zones. Mean dripwater and groundwater $\delta^{18}O$ values (-6.4‰ and -6.2‰, respectively) are lower than the weighted-mean value for $\delta^{18}O_{precip}$ (-5.4‰), indicating preferential recharge of rainwater with low $\delta^{18}O$ values. The mean precipitation-weighted $\delta^{18}O_{precip}$ value for the months of August to October is -6.3‰. Assuming that the groundwater isotopic composition is the amount-weighted average of rainwater that actually recharges the system, this indicates that recharge occurs predominately during the wet season and is a result consistent with previous work on Guam (Jocson et al., 2002; Jones and Banner, 2003; Partin et al., 2012) and other tropical carbonate islands (Jones and Banner, 2003). Further, preferential recharge during the wet season is consistent with the conceptual model in which water recharging the cave, likely during the wet season, has not experienced significant evaporation, but is carrying with it dissolved salts from the evaporation of previous rainfall, likely during the dry season, that did not recharge the cave.

Cave dripwater $\delta^{18}O$ values exhibit an observable decreasing trend during the last one to two years at each site (Fig. 1.6), with a statistically significant (p-value< 0.001, Supplemental Table S6) decrease in three of the four sites. These trends occur despite the absence of a significant trend in precipitation $\delta^{18}O$ values or annual precipitation-weighted mean values of $\delta^{18}O_{precip}$ from recharge months (i.e., August, September, and October) (Fig. 1.6). The nature of rainfall, however, is notably different before and after the 2013 wet season, with higher cumulative monthly rainfall totals during dry and wet seasons following the 2013 wet season (Fig. 1.6). More-intense precipitation may promote greater runoff and enhance the recharge bias toward isotopically lighter precipitation (Jones and Banner, 2003). Furthermore, a marked decrease in the extent to which drip rates decline over the dry season after 2013 indicate that such changes in precipitation amount translate to increased recharge and water in vadose zone storage.

Cave dripwater $\delta^{18}O$ values are slightly more variable at fracture-supplied sites relative to diffuse-supplied sites (Fig. 1.7), and $\delta^{18}O$ values at diffuse-supplied sites are slightly lower relative to fracture-supplied sites. These results are consistent with the flow paths along dissolution enhanced fracture networks facilitating more direct infiltration of water relative to diffuse flow paths, leading to greater reflection of the isotopic variability occurring in $\delta^{18}O_{precip}$ values and less of a recharge bias. That is, the difference in mean values between sites supplied by fracture vs diffuse flow paths (Fig. 1.7B and 1.7C) reflects differences in the sensitivity of these flow paths to changes in hydrologic conditions at the surface.

1.5 Conclusions

Analysis of the spatial and temporal variability of geochemical and isotopic compositions of cave dripwater and groundwater over an interval that spanned a transition from dry to wet conditions independently reinforces the existing conceptual model of recharge and groundwater flow in the NGLA. This model, up to now, has been based mainly on observations of physical hydrogeology, unconditioned by geochemical observations. Specifically, we find geochemical evidence that:

- The sensitivity of the freshwater lens to intra- and inter-annual changes in recharge is spatially variable, as evidenced by the geochemical variability observed in wells distributed across the study area (Figs. 1.1, 1.3, and 1.5).
- Groundwater compositions are influenced by water-rock interaction and mixing between recharging meteoric water and seawater (up to 1%), as evidenced by the ability of

geochemical and isotope modeling to explain observed groundwater compositions (Figs. 1.3 and 1.5).

- Dissolution enhanced fracture networks constitute preferential recharge pathways, as evidenced by distinct geochemical and isotopic variability of fracture-supplied and diffuse-supplied sites (Figs. 1.4, 1.6, and 1.7).
- Recharge is sensitive to inter-annual changes in precipitation amount and intensity, as evidenced by intra- and inter-annual variations in the geochemical and isotopic compositions of groundwater (Figs. 1.4 and 1.6).
- Recharge predominantly occurs during the wet season based on the coincidence of average groundwater $\delta^{18}O$ values with the amount-weighted average $\delta^{18}O_{precip}$ values occurring during the wet season (Figs. S1.2 and 1.6).
- The freshwater lens is, isotopically and geochemically, buffered from the hydroclimatic variability that occurred during the study. This is supported by the limited variability in isotopic and geochemical compositions of both cave dripwater and groundwater relative to the magnitude of intra- and inter-annual variability in precipitation amount and precipitation isotopic compositions (Figs. 1.4 and 1.6).

1.6 Acknowledgements

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1.7 Figures

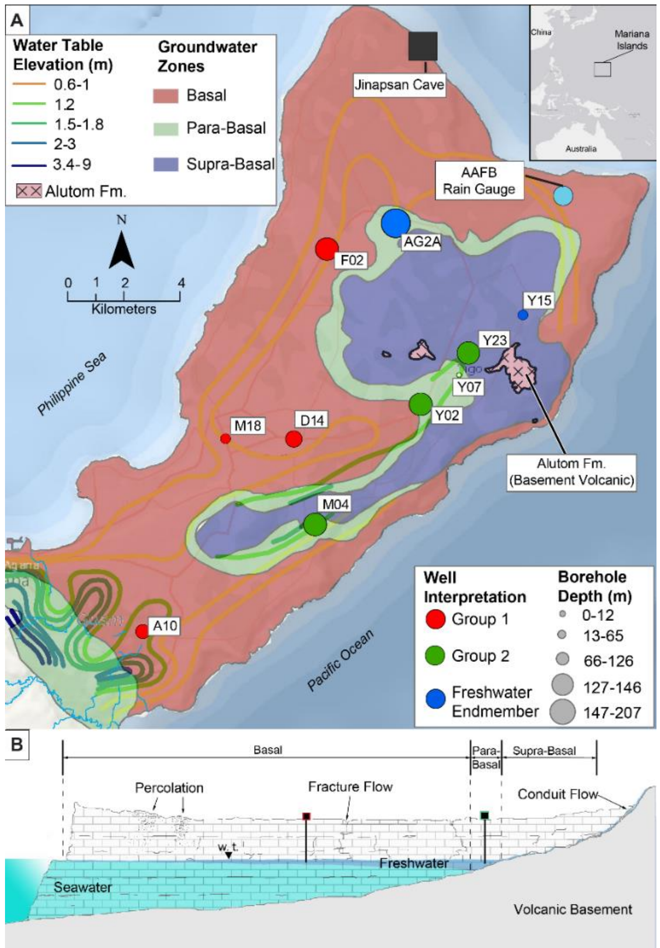

Figure 1.1 (A) Map of the groundwater zones of the NGLA and locations of sampled wells with size and color of the symbols reflecting depth and geochemical interpretations. Inset map (upper right) to reference location of the Mariana Islands, in which Guam is located. (B) Composite cross-section (not to scale) depicting wells accessing basal (red), and para-basal (green) groundwater zones. Figure modified from Vann et al. (2014). The base map sources are from ESRI, GEBCO, NOAA, and other contributors. Potentiometric lines were obtained from the Water and Environmental Research Institute of the Western Pacific *Digital Atlas of Northern Guam*.

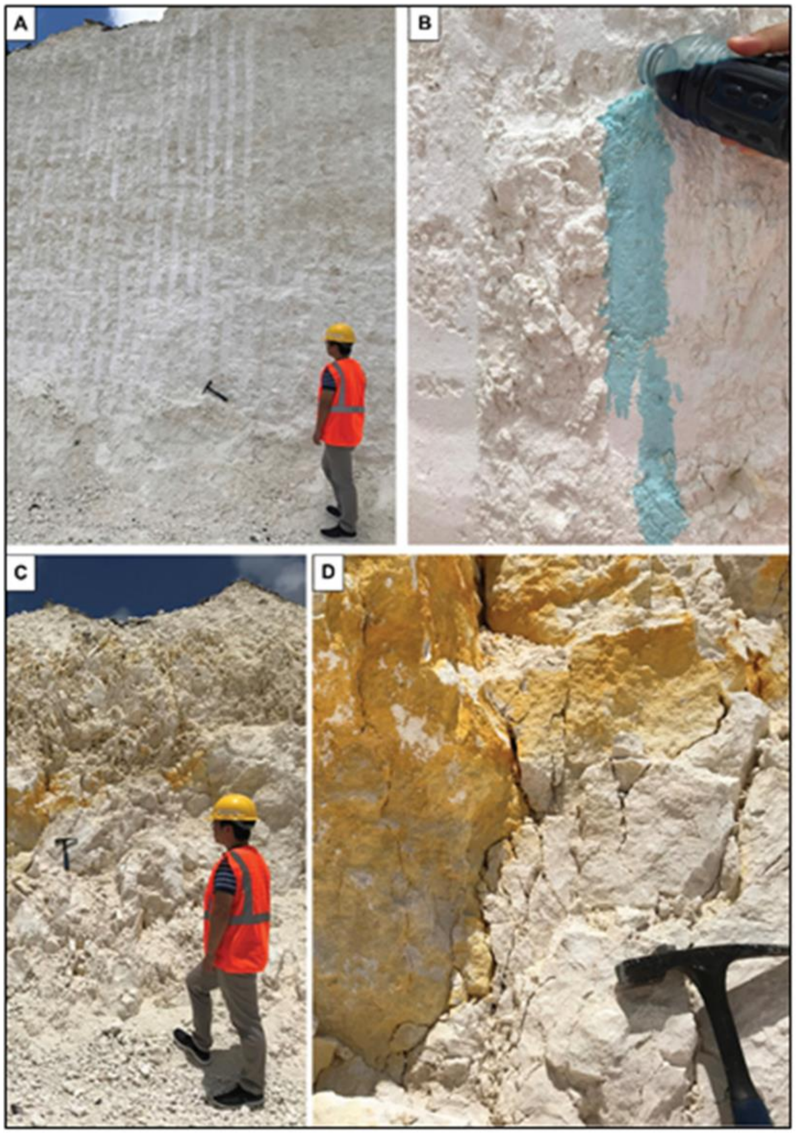

Figure 1.2 Images of the Barrigada Limestone showing the poorly cemented, unfractured zone (A and B) and the cemented, coarsely friable, and fractured zone (C and D) taken at the Dededo Public Works Quarry, Guam. Rapid absorption is demonstrated with blue-colored water in (B). Staining shown in (D) is attributed to frequent percolation by vadose water carrying iron-rick minerals originating in soil.

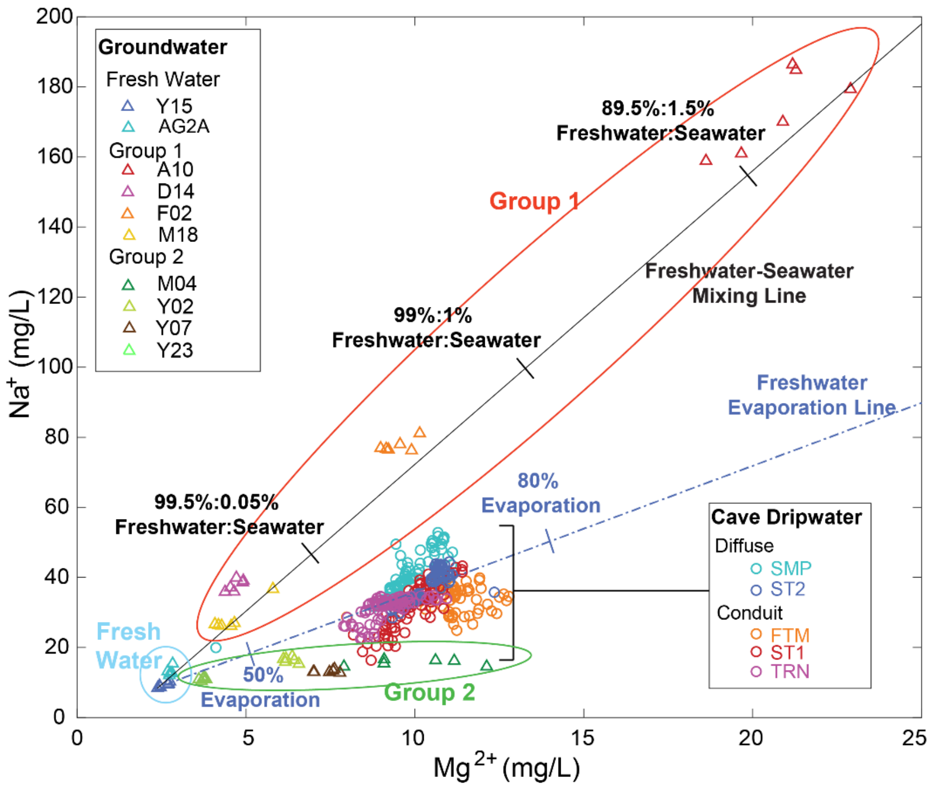

Figure 1.3 Bivariate plot of cave dripwater and groundwater Mg^{2+} and Na^{+} concentrations with model curve of freshwater-seawater mixing and evapo-concentration of freshwater. Freshwater represented by groundwater with lowest Na^{+} (8.4 ppm) and Mg^{2+} (2.4 ppm) concentrations. Seawater represented by Na^{+} and Mg^{2+} concentrations of 10,800 and 1,290 ppm, respectively (Turekian, 1968).

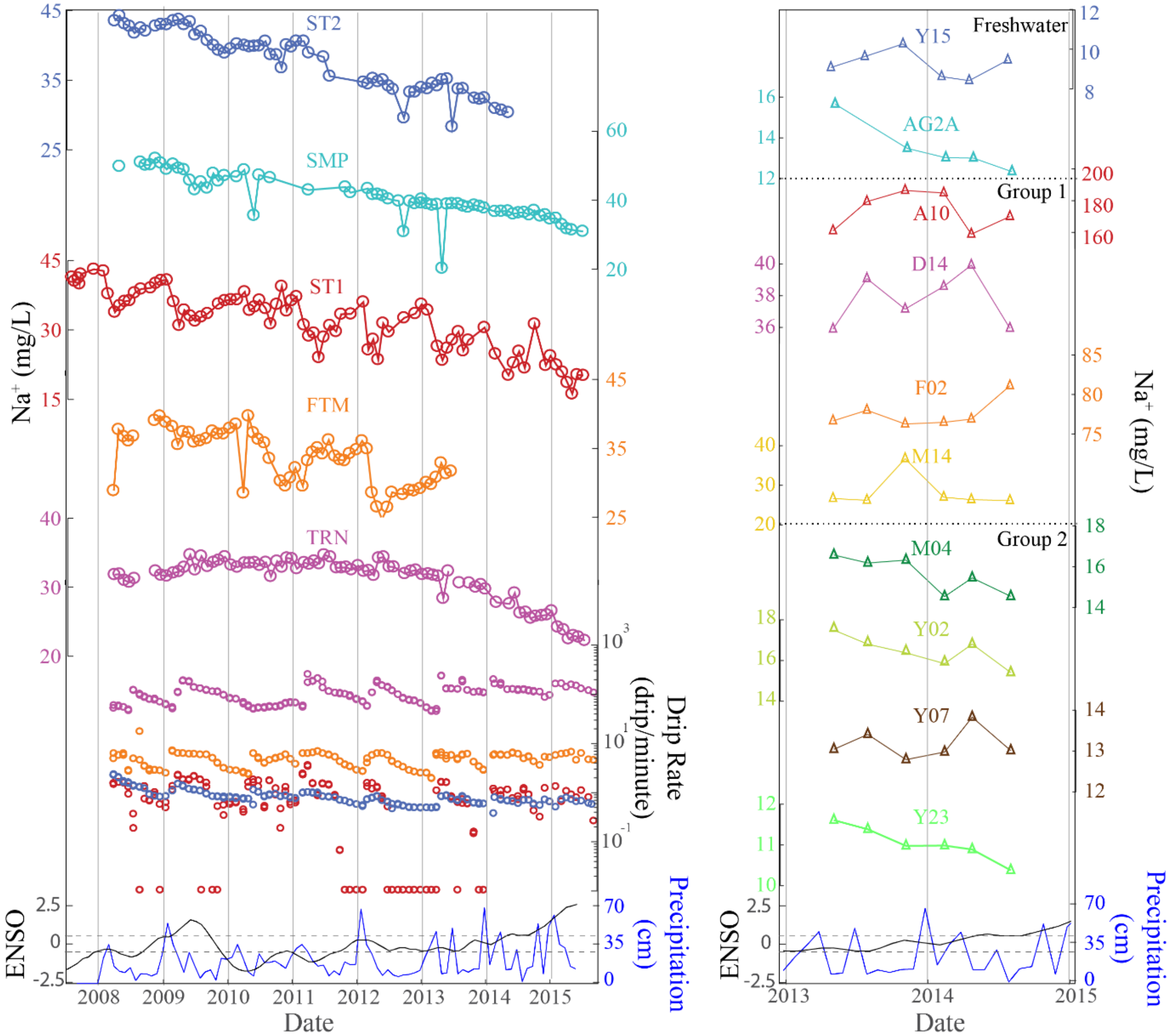

Figure 1.4 Time series of cave dripwater (left panel) and groundwater (right panel) Na^+ concentrations with cave drip rate, monthly precipitation (blue), and the El Niño Southern Oscillation 3.4 Index (black). Intra- and inter-annual variations in Na^+ concentrations are more pronounced at dripwater sites relative to groundwater wells.

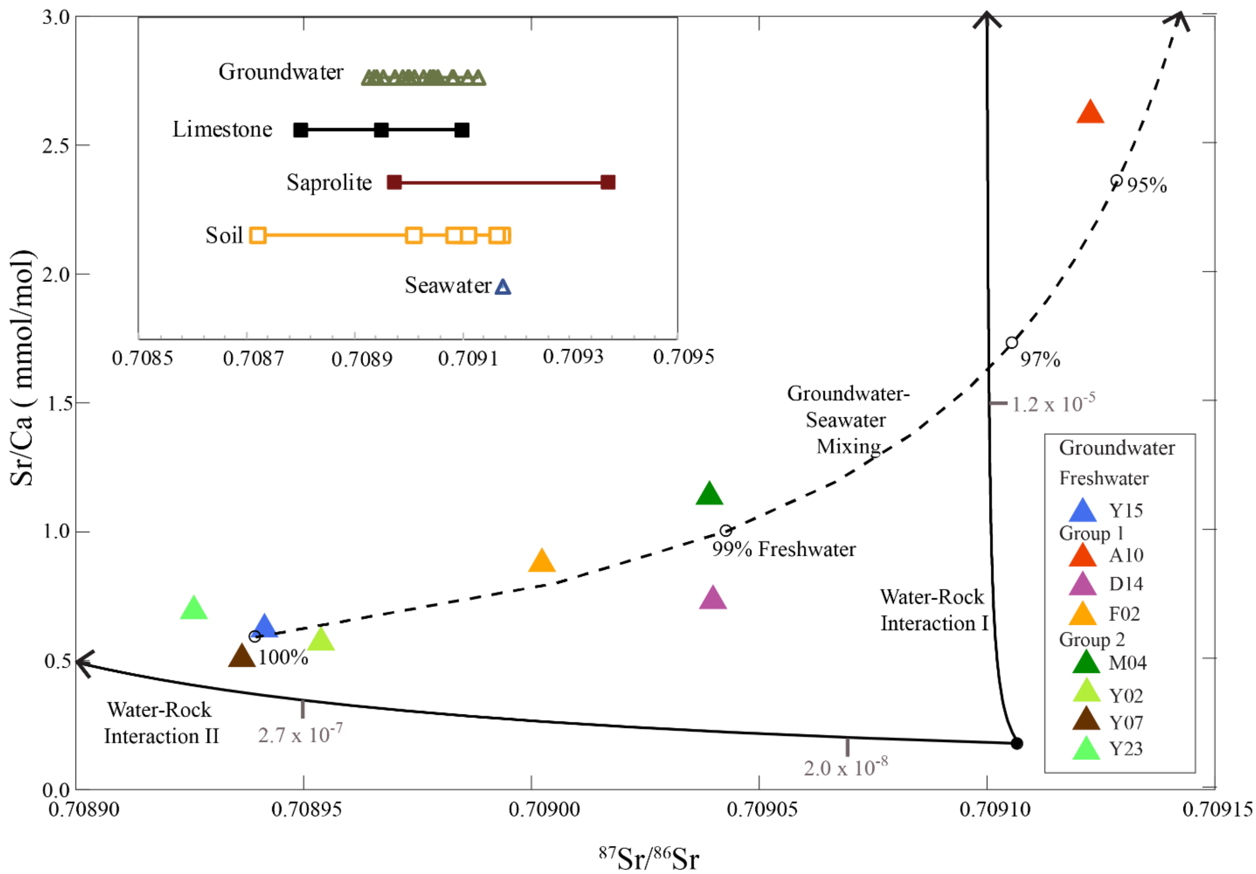

Figure 1.5 Measured groundwater Sr/Ca and $^{87}Sr/^{86}Sr$ values with modeled (solid curves) evolution of groundwater compositions via water-rock interaction from an initial composition (solid black circle). The inset graph represents the range of $^{87}Sr/^{86}Sr$ values for the study area measured as a part of this study (groundwater, saprolite, and soil) and retrieved from the literature (seawater and bedrock). Fluid-rock ratios (molar) are given along the curves (grey ticks). Mixing between groundwater and seawater is also shown (dashed curve). See Methods for discussion of modeled curves.

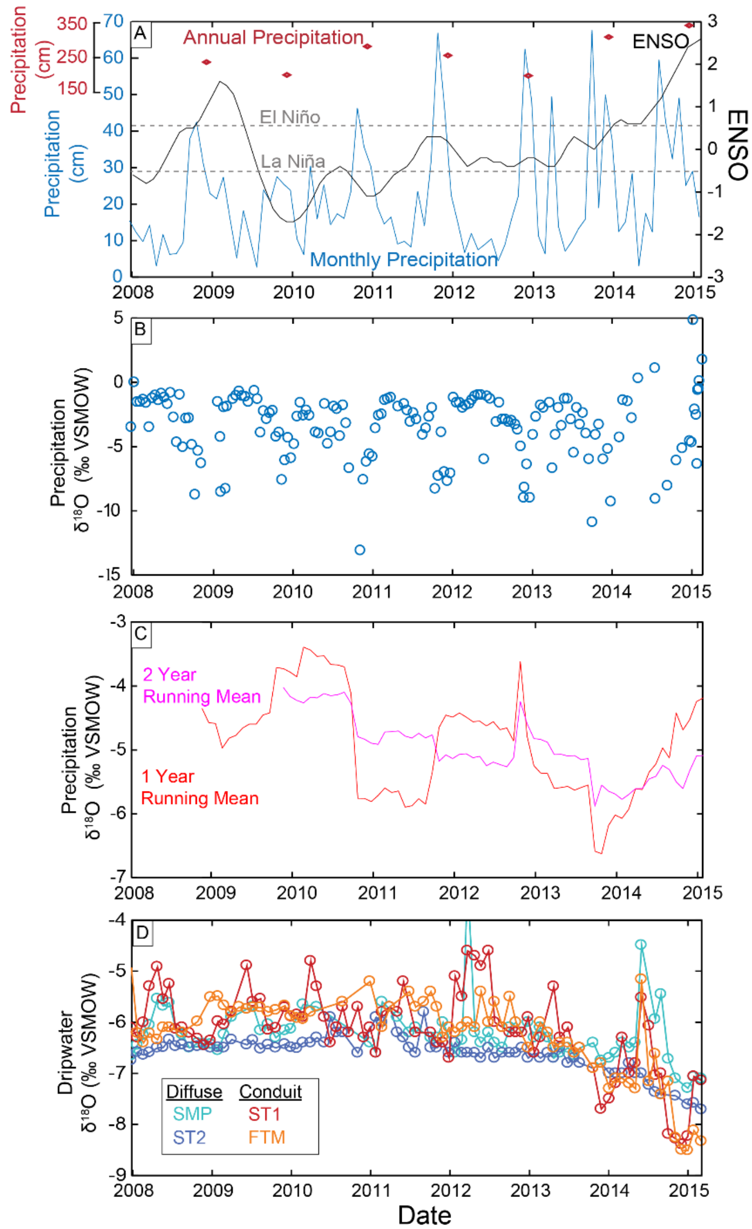

Figure 1.6 (A) Time series of monthly (blue) and annual (red) cumulative precipitation for Guam with the El Niño Southern Oscillation 3.4 index (black). (B) Bi-weekly $\delta^{18}O_{precip}$ values. (C) One- and two-year running mean for annual precipitation-weighted $\delta^{18}O_{precip}$ values during the recharge months (i.e. August, September, and October). (D) Monthly cave dripwater $\delta^{18}O$ values.

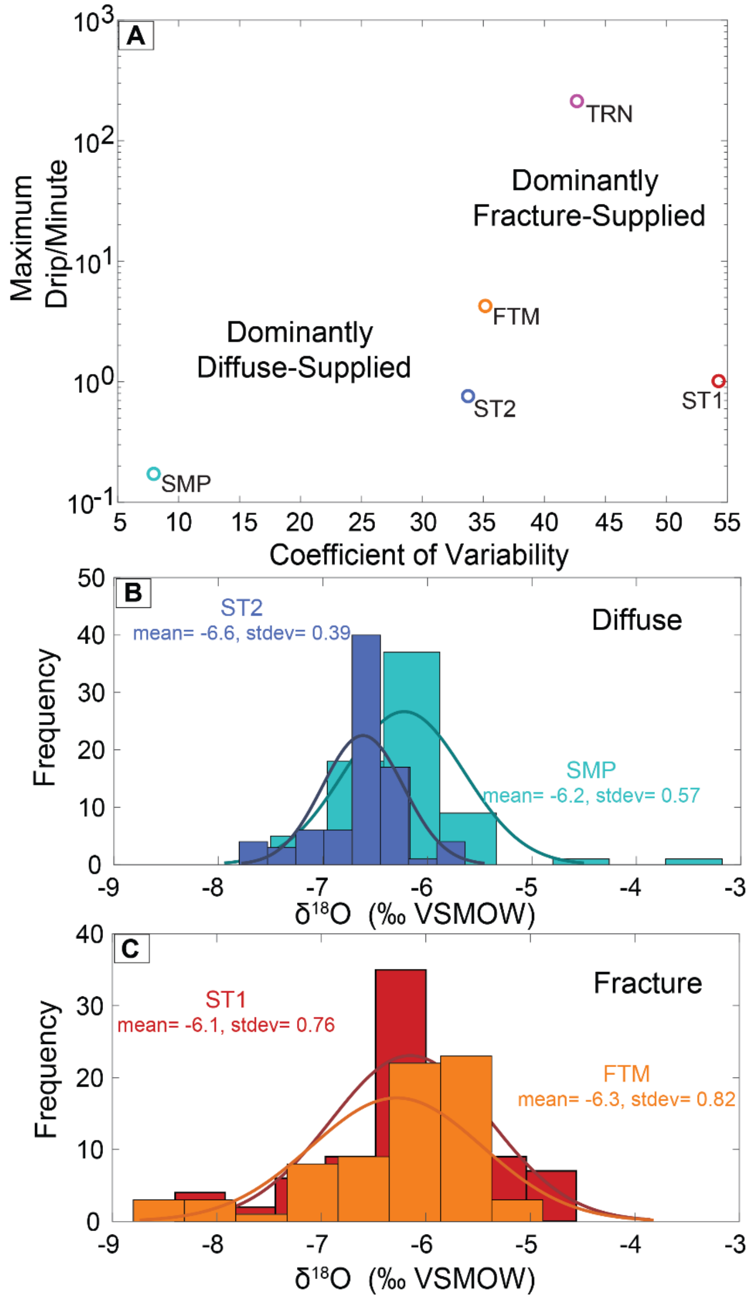

Figure 1.7 (A) Drip-site categorization based on maximum drip rate and coefficient of variability. (B and C) $\delta^{18}O$ distribution for dominantly diffuse- and fracture-supplied dripwater sites, respectively.

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*Chapter II

Tracking the sources and processes of impacts on stream water evolution in a rapidly urbanizing carbonate watershed in Austin, TX

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2.0 Abstract

Quantifying urban development impacts on freshwater quality and quantity is critical, especially as growing populations concentrate in urban centers and with climate change projections of increased hydrologic extremes. We investigate geochemical processes through which municipal (supply and waste) water impacts stream and spring water compositions within the carbonate Bull Creek watershed (Austin, Texas), which exhibits a distinct geographic divide between urban development and rural land. $^{87}Sr/^{86}Sr$ and elemental variations are assessed for waters sampled from rural and urban sites to quantify relative influences of natural versus municipal water. Higher $^{87}Sr/^{86}Sr$ values for urban sites relative to rural sites can be accounted for by two models: (1) water leakage from municipal infrastructure and/or irrigation, or (2) ion exchange as precipitation infiltrates through soils with varying $^{87}Sr/^{86}Sr$. Irrigated soils have higher $^{87}Sr/^{86}Sr$ values than unirrigated soils, indicating that municipal water resets soil compositions, and that process (1) is a dominant driver of urban stream and spring water evolution. Fluid mixing models indicate that urban waters consist of 50% - 95% municipal water. Water-rock interaction modeling documents the geochemical evolution of infiltrating municipal water, whereby municipal water infiltrates as groundwater and undergoes diagnostic extents of water-rock interaction with the carbonate bedrock. These results are compared with regional phreatic and vadose groundwater compositions to infer local flow pathways and relative groundwater residences times of both municipal and rural water. This study advances our understanding of the significance of municipal water influences on urban stream water and soil compositions, and provides a geochemical modeling framework that quantifies the evolution of infiltrating municipal water within carbonate watersheds and aquifers.

2.1 Introduction

Documenting urban development impacts on freshwater resources is critical for ensuring resiliency of both the quality and quantity of freshwater, which will become increasingly important with rapid population growth (U.N. Dept. of Economic and Social Affairs, 2017) and climate change projections of increased hydrologic extremes for the 21st century (IPCC, 2014). The global population is expected to increase from 6.9 billion in 2010 to 9.8 billion in 2050 (U.N. Dept. of Economic and Social Affairs, 2017; U.N. Dept. of Economic and Social Affairs, 2014). 66% of this growing population is projected to be concentrated in urban areas, which will make the provisioning (e.g., quantity, quality, and distribution) of freshwater an acute challenge in many regions (McDonald et al., 2011). The study of urban hydrology has increased in the past several decades to address the challenges in management of sustainable water quantity and quality. These studies have characterized urban hydrologic phenomena, including increased runoff amounts and flashy discharge due to impervious cover (e.g., Leopold, 1968; Boyd et al. 1993; Schueler, 2000; Ragab et al., 2003; Glick, 2009; Shuster et al., 2011), the degradation of stream water quality from storm water drainage and leakage of water main networks (e.g., Walsh et al., 2005; Reynolds et al., 2003; Hamel et al., 2013), and the decrease in sensitive aquatic habitat in urban watersheds (Bendik et al., 2014). Studies that focus on the interaction between municipal water networks and the natural hydrologic cycle have estimated urbanization effects on local and regional groundwater recharge, and have highlighted mechanisms by which urbanization changes surface and subsurface flow processes (e.g., Lerner 1990; Berg et al., 1996; Yang et al., 1999; Garcia-Fresca and Sharp, 2005; Sharp, 2010; Bhaskar and Welty, 2012; Passarello et al., 2012; Bhaskar et al., 2016; Minnig et al., 2018). Studies that provide evidence for municipal water influence on natural surface and groundwater composition (via leakage and

/or irrigation) have shown discrete measurements of municipal water indicators, yet these studies do not address the flow pathways or groundwater residence times of municipal water (Christian et al., 2011; Senison et al., 2013; DeMott, 2006; Reynolds and Barrett, 2003, Pu et al., 2014). Quantifying the geochemical evolution of infiltrating water can inform relative groundwater residence times, the interaction between local to regional hydrogeologic units, and can be used to infer subsurface flow pathways (e.g., Wong et al., 2014). Here we seek to quantify: 1) the extent that infiltrating municipal water mixes with natural groundwater and stream water, and how it interaction with carbonate bedrock, 2) the relative depths to which municipal water infiltrates, and 3) the relative groundwater residence times of infiltrating municipal water with respect to regional phreatic and vadose groundwater. Here we assess for the first time the geochemical evolution of municipal water upon its infiltration into a carbonate system using spatial variations of stream and spring water geochemical composition in a semi-urbanized watershed. We then use this evolution to estimate the relative extents of water-rock interaction among the rural and urban stream and spring water samples. The extent of water-rock interaction for a given stream or spring water is compared to regional groundwater data where vadose and phreatic flow pathways are delineated. The comparison of water-rock interaction between this study and regional phreatic (i.e., largest extent of water-rock interaction) and vadose zone (i.e., smallest extent of water-rock interaction) water is then used to infer relative groundwater residence times of municipal (supply and waste) water.

This study focuses on impacts to stream and spring water compositions within a single carbonate watershed (Bull Creek watershed) in the area of Austin, Texas, which exhibits a sharp geographic divide (i.e., steep gradient) between urban development and rural land. This sharp divide offers an opportunity to understand endmember (e.g., municipal water) processes that may be more obscured in other area watersheds, which have less well delineated distributions of urban and rural land (Figs. 2.1 and 2.2).

Regional demographic projections in central Texas indicate rapid urbanization has occurred and will continue in the coming decades (Texas Demographic Center, 2019), and understanding the geochemical evolution of stream and spring water in this semi-urbanized watershed will provide insight into the impacts to freshwater quality and quantify the urban hydrologic cycle as development continues. The population of Austin increased from 576,407 in 1990 to 790,390 in 2010 (a 37% increase), and is expected to reach 2 million by 2050 (U.S. Census Bureau 1990; Texas Demographic Center, 2019). Population growth in urban centers, coupled with climate change projections of an intensifying hydrologic cycle (Hayhoe, 2014; Swain and Hayhoe, 2015), pose significant challenges to water resource (e.g., Banner et al, 2010; Breyer at al., 2018) and habitat (e.g., Bendik et al., 2014) management that requires a dynamic understanding of the altered quantity and quality of water within the urban hydrologic cycle. Austin area municipal system losses (i.e., leakage) and irrigation demands account for 12% and 21%, respectively, of the annual city water production. Losses are based on the difference between pumpage from water treatment plants and the annual billable consumption (Joe Smith, City of Austin, personal comm.). The influence that municipal (supply and waste) water has on natural geochemical compositions can be quantified using endmember isotopic (e.g., $^{87}Sr/^{86}Sr$) and geochemical tools (Christian et al., 2011; DeMott, 2006; Senison, 2013).

Previous studies within the Bull Creek watershed have 1) characterized an increase in stream water nutrients (Ging, 1994; Duncan et al., 2010), 2) inferred temporal shifts in the geochemical composition of spring discharge toward municipal water (DeMott, 2006), and 3) measured declines in an endangered salamander population within the urbanized areas (Bendik et al., 2014). Here we use geochemical and isotopic ($^{87}Sr/^{86}Sr$) variations in stream water, spring water, municipal supply and waste water, and soils and bedrock to assess and quantify the evolution of stream and spring water compositions sampled across the watershed's urban and rural land (Fig. 2.2) Tracking the geochemical processes that control stream and spring water evolution along Bull Creek's urban and rural land is likely to yields insight to analogous processes in both rural and densely urbanized carbonate watersheds.

Stream and spring water in the Bull Creek watershed was sampled intermittently (quarterly to annually) from 2010 to 2013. In addition to quantifying the geochemical evolution of urban stream and spring water, we test whether the natural variability of soil is a source of high $^{87}Sr/^{86}Sr$ values for urban stream water (Christian et al., 2011), which would discount $^{87}Sr/^{86}Sr$ as a tracer for municipal water. We test this hypothesis through a comparative study of soils across the urbanization gradient, which shows a discrete increase in $^{87}Sr/^{86}Sr$ values from unirrigated (i.e., natural) soils to soils irrigated with municipal water.

2.2 Study Area

2.2.1 Spatial and land use setting

The Bull Creek watershed occupies 82 km^2 of northwest Austin (Fig. 2.1). The catchment area is considered semi-urbanized, with urban development (largely single-family homes) occupying approximately half of the watershed, north of the main stream channel (Fig. 2.2). The urbanized region of the watershed has experienced increased urban development over the past two decades, and the population is projected to increase from 44,000 in 2000 to 70,000 by 2030 (City of Austin – Watershed Protection Department Masterplan, 2001). The undeveloped region of the watershed is protected from urbanization to maintain habitat for endangered species and to preserve the quality and quantity of spring discharge along the tributary canyon walls that provide perennial habitat for sensitive aquatic organisms (Balcones Canyonlands Preserve, 1996).

2.2.2 Hydrogeologic setting

The Bull Creek watershed is made up of Trinity and Edwards Groups (Cretaceous), with carbonate bedrock including (from oldest to youngest) the Glen Rose, Walnut, Comanche Peak, and Edwards Limestone (Fig. 2.2A). The Edwards Limestone is the principal aquifer for much of central Texas, and provides drinking water for cities both north and south of Austin. The Edwards aquifer outcrops in the study area (60-100 m thick), and is made up of chert-rich, rudist-bearing, dolomitic limestone. The presence of vugs, solution collapse zones, caverns, and fractures make the Edwards Limestone highly transmissible, both locally and regionally. The underlying geologic units locally vary between the thin (6 m) Comanche Peak Limestone, and the Walnut Formation (up to 40 m thick). The Comanche Peak Limestone is a fine-grained fossiliferous limestone with interbedded marl and shale (Brune and Duffin, 1983) that pinches out in the northwestern region of the Bull Creek watershed (Fig. 2.2). The Walnut Formation is a thick (up to 40 m) medium-grained fossiliferous limestone that underlies the Edwards formation through much of the watershed. The Walnut formation is considered a confining unit, although the presence of permeable shell beds may transmit groundwater (Brune and Duffin, 1983). The Glen Rose limestone (Trinity Group) is a thick (200 m) package of alternating limestone, dolomite, and marl beds (Brune and Duffin 1983). The Glen Rose limestone is considered a low-permeability unit that yields small amounts of fresh to slightly saline water (Brune and Duffin, 1983; Wong et al., 2014). Seeps and springs are observed throughout the Edwards-Walnut and Glen Rose formations in the Bull Creek watershed. These seeps and springs provide baseflow to tributary channels throughout the watershed (Geismer, 2011).

The topography within the Bull Creek watershed varies from 5-15% rolling slopes (Geismar, 2001) to 100 m deep canyons. There are four primary soils that overly the carbonate bedrock—Brackett, Speck, Tarrant, and Volente soils (Fig. 2.2B). Brackett and Tarrant soils occupy 89% of the watershed. Both soil types are thin (0-50 cm), well-drained, gravelly clay loam and stony clay material. Volente soils are well-drained, thick (55-130 cm), and range from silty clay to silty clay loam that occurs adjacent to stream channels (Fig. 2B, USDA 1974). The Speck soil occupies 2% of the surface near the northern watershed boundary, and is considered moderately thick (45 cm) clay loam. It should be noted that "Urban Land" soils (e.g., highly altered and obscured; USDA, 1974) occur in other Austin area watersheds, but are not documented within the Bull Creek watershed. Recent field observations, however, show unconformities within soil profiles where landscaping is prevalent.

2.3 Methods

The extent of urban development associated with each stream and spring water sample location was delineated based on calculated subwatershed areas in ArcGIS (ESRI, 2017). Subwatersheds were delineated for each site following the methods of Maidment (2002), and percent impervious cover and road density were calculated based on the spatial extent within each subwatershed (from City of Austin, 2010, Land Use geodata). The stream and spring water sampling sites selected for this study were classified as urban or rural based on percent estimated impervious cover and road density within each subwatershed. Here we define urban sites with either greater than 25% impervious cover or greater than 0.002 m^{-1} road density within the subwatershed, whereas rural sites have less than 25% impervious cover and 0.002 m^{-1} road density within the subwatershed. Stream and spring water samples were collected under baseflow conditions in August 2010, April 2011, and quarterly from July 2012 to June 2013, spanning 21 urban and seven rural sites (Fig. 2.2). Samples were collected in precleaned HDPE Nalgene bottles and decanted with a 0.45 micron polypropylene syringe filters into precleaned HDPE plastic vials for anion analysis, and acid-cleaned vials for cation and Sr-isotope ($^{87}Sr/^{86}Sr$) analysis. Water samples for cation and $^{87}Sr/^{86}Sr$ analysis were acidified with concentrated ultrapure HNO_3. Soil samples (n = 20) were collected for $^{87}Sr/^{86}Sr$ analysis using precleaned plastic trowels from 5 –15 cm depth, and were classified by irrigated (i.e., urban) and unirrigated (i.e., natural) soils based on field-observed presence of irrigation systems and surveying of landowners. Soil samples were leached using ammonium acetate to extract exchangeable ions from grain surfaces, to simulate the natural interaction of infiltrating water with soils. Carbonate bedrock samples were first treated with ammonium acetate to minimize trace element leaching of noncarbonate minerals, then the bedrock sample was dissolved using acetic acid. Both soil and carbonate bedrock leachate extractions followed a method modified from Montañez et al. (1996).

Water samples collected for major ion geochemistry in 2010 and 2011 were analyzed by the Lower Colorado River Authority, in partnership with the City of Austin - Watershed Protection Department. Municipal water samples were collected from residents within the Bull Creek watershed (Fig. 2.2), while municipal waste water samples were collected by the City of Austin - Watershed Protection Department from city-wide waste water treatment plants. Water, soil, and bedrock samples collected in 2012 and 2013 were analyzed at The University of Texas at Austin, Department of Geologic Science (UT DGS), and the respective analytical methods are summarized below. Stream and spring water Cl, SO_4, and NO_3 concentrations were determined using Waters 501 High Performance Liquid Chromatograph (HPLC). F was measured using a LaF_3 Ion Selective Electrode. The percent difference between replicate samples (n = 23) for Cl, SO4, NO_3, and F were within 10%, with one exception, for which NO_3 had an anomalous uncertainty of 25%. Cation concentrations were analyzed using an Inductively Coupled Plasma Quadrupole - Mass Spectrometer. Analytical uncertainty for Ca, Mg, Na, and Sr was 0.13, 0.04, 0.04, and 0.02 ppm, respectively, based on twice the standard error of sample replicate analyses of the internal standard. The mean percent difference between replicate samples ($n = 7$) for Ca, Mg, Na, and Sr are within 4%. Detection limits for anions and cations were one to five orders of magnitude below sample elemental concentrations. Charge balances for stream and spring water samples ranged from ±0.8% to ±10.3%, with most (89%) of the samples less than ±5%. Water, soil leachate, and limestone bedrock $^{87}Sr/^{86}Sr$ values were determined following the methods of Banner and Kaufmann (1994) and Musgrove and Banner (2004) using a Thermo Triton Thermal Ionizing Mass Spectrometer. The analytical uncertainty is +/- 0.000015 for reported $^{87}Sr/^{86}Sr$ values, based on 2-sigma (2σ) standard NBS-987 measurements ($^{87}Sr/^{86}Sr = 0.710271$). Field and laboratory blank analyses contained 130 pg and 4 to 12 pg of Sr, respectively, which are negligible relative to the minimum amount of analyzed Sr (2 μg).

The geochemical and isotopic evolution of stream and spring water due to endmember mixing and water-rock interaction are modeled following Banner et al. (1989), Banner and Hanson (1990), Banner et al. (1994), and Musgrove and Banner (2004). We consider endmember mixing between representative municipal supply water and rural water (e.g., samples with the highest and lowest $^{87}Sr/^{86}Sr$ values, respectively), which is calculated by mass balance between endmember $^{87}Sr/^{86}Sr$ values and Sr concentrations. Water-rock interaction processes are modeled based on mass-balance relationships between endmember (e.g., Cretaceous limestone, municipal supply water) elemental and isotopic ratios. We model two distinct geochemical processes for municipal water interacting with calcite and dolomite: 1) dissolution (Fig. 2.6) and 2) recrystallization (i.e., dissolution and re-precipitation; Fig.2.7). The dissolution model uses iterative mass-balance calculations to simulate incremental increases of Ca and Sr from limestone into solution. The recrystallization model uses iterative mass-balance calculations to simulate a given volume of water passing through progressively increasing increments of limestone bedrock. In the recrystallization model, we assume that during each iteration the volume of water attains equilibrium with the calcite and dolomite in the limestone bedrock (Banner et al., 1989; Banner et al., 1994; Musgrove and Banner, 2004).

2.4 Results

2.4.1 Stream water and endmember $^{87}Sr/^{86}Sr$ variation

In the Austin area, natural groundwater and stream water $^{87}Sr/^{86}Sr$ values (mean $^{87}Sr/^{86}Sr$ = 0.7079; Christian et al., 2011) are similar to values for Cretaceous seawater ($^{87}Sr/^{86}Sr$ = 0.7072–0.7080; Koepnick et al., 1985), likely reflecting Sr sourced by limestone bedrock (Fig. 2.2A). In contrast, municipal supply water is withdrawn from the Colorado River, which distinctly high $^{87}Sr/^{86}Sr$ values (mean $^{87}Sr/^{86}Sr$ = 0.7090; Christian et al., 2011). Elevated $^{87}Sr/^{86}Sr$ values for the Colorado River reflect the dissolved contribution of Sr from Precambrian granitic and metamorphic rocks that outcrop approximately 100 km upstream of Austin in the Llano uplift region (Christian et al., 2011). The dissolved Sr with high $^{87}Sr/^{86}Sr$ values from the Precambrian rock is discharged to the Colorado River via tributary channels, such as the Llano River ($^{87}Sr/^{86}Sr$ = 0.7102, n = 1; Christian et al., 2011).

We use local and regional $^{87}Sr/^{86}Sr$ values to identify endmembers within the Bull Creek watershed (Fig. 2.3). Measured $^{87}Sr/^{86}Sr$ values for Bull Creek stream and spring water samples had a narrow range for rural samples ($^{87}Sr/^{86}Sr$ = 0.7078 – 0.7081), while urban samples had a larger range that extended to higher values ($^{87}Sr/^{86}Sr$ = 0.7077 – 0.7088). We consider three endmembers that may account for observed variability in the watershed: 1) rural stream and spring waters (“rural waters” herein; $^{87}Sr/^{86}Sr$ = 0.7078 – 0.7080), 2) municipal supply water ($^{87}Sr/^{86}Sr$ = 0.7091– 0.7095) and 3) waste water ($^{87}Sr/^{86}Sr$ = 0.7079 – 0.7090; Fig. 2.3). The low concentration of Sr in rainwater (mean Sr = 0.006 ppm; Christian et al., 2011) is negligible relative to the other endmembers and is not considered further as it is unlikely to contribute measurable Sr to the watershed. Other sources of high $^{87}Sr/^{86}Sr$ values (e.g., $^{87}Sr/^{86}Sr > 0.7085$) to Austin stream and spring water have been hypothesized to include soils in the watersheds with high $^{87}Sr/^{86}Sr$ values (Christian et al., 2011). Our results show a distinct increase in soil leachate $^{87}Sr/^{86}Sr$ values (Fig. 2.3) from unirrigated (i.e., natural) soil ($^{87}Sr/^{86}Sr$ = 0.7079 – 0.7084) to soils irrigated with municipal supply water ($^{87}Sr/^{86}Sr$ = 0.7085 –0.7091).

2.4.2 Comparison of endmember geochemical compositions

The geochemical composition of endmembers are distinct, with respect to major ions (e.g., Ca, Na, Cl, and HCO_3; Table 1). Municipal supply water is a Mg-HCO_3 type water, although HCO_3 concentrations are relatively low (60 – 76 ppm) compared to Bull Creek rural water (308 – 359 ppm; Table 1). Both the rural and urban stream and spring water samples are Ca-HCO_3 type waters, but the range of Ca concentrations is higher in the urban stream and spring waters (67 – 166 ppm) relative to the rural waters (85 – 104 ppm; Table 1). Na and Cl concentrations (Table 1; Fig. 2.4) are elevated in both the municipal waste water (43 - 105 ppm and 57 - 167 ppm, respectively) and urban stream and spring water samples (11–74 ppm and 19–93 ppm, respectively), relative to municipal supply water (18 – 31 ppm and 27 – 44 ppm, respectively) and the rural waters (7 – 11 ppm and 16 – 26 ppm, respectively). The urban stream and spring water Na and Cl concentrations span the range between the lowest concentrations observed among the rural water sites and the highest concentration in the municipal waste water samples (Fig. 2.4). The municipal waste waters show a higher range of Na concentrations relative to Cl concentrations, such that many of the samples lie above the 1:1 (Cl:Na) line (Fig. 2.4).

2.4.3 Geochemical modeling

Fluid mixing and water-rock interaction models were used to assess geochemical processes that account for the variations observed in Bull Creek stream and spring water compositions. Two sets of endmembers were used for the fluid mixing models to portray the range of water compositions that may result from fluid mixing. Fluid Mixing Line I (Fig. 2.5) uses high $^{87}Sr/^{86}Sr$ endmember compositions, whereas Fluid Mixing Line II uses low $^{87}Sr/^{86}Sr$ endmember compositions (Fig. 2.5). Thus, the fluid mixing models represent the full range of mixing between rural and municipal supply endmembers. Results show that urban stream and spring waters consist of up to 95% municipal water (Fig. 2.5). We identified two urban stream and spring water populations (Fig. 2.5) differentiated by low Sr concentration (< 0.27 ppm) (hereafter “low Sr urban waters”), and high Sr concentration (> 0.44 ppm) (hereafter “high Sr urban waters”). Approximately half (55%) of the urban waters are not accounted for the by the mixing models, particularly where the measured compositions fall above Fluid Mixing Line I (and below the model trend for limestone recrystallization) or below Fluid Mixing Line II (and above the model trend for limestone dissolution; Fig. 2.5). The low Sr urban waters have distinctly higher $^{87}Sr/^{86}Sr$ values ($^{87}Sr/^{86}Sr$ >0.7082) than either rural or high Sr urban waters, and consist of approximately 50% – 95% municipal water. In contrast, the high Sr urban waters have distinctly lower $^{87}Sr/^{86}Sr$ values ($^{87}Sr/^{86}Sr$ < 0.7082) and mixing results show a notable small municipal component (< 50%).

Sr and Ca concentrations are quite variable in Bull Creek stream and spring waters (Fig. 2.6). Ca and Sr concentrations for municipal (supply and waste water) endmember compositions are notably low relative to the rural and urban stream and spring waters (Fig. 2.6). Both the high and low Sr urban waters have a relatively large range of Ca concentrations (75 - 146 and 67 - 166 ppm, respectively; Fig. 2.6), but exhibit contrasting Sr concentrations (high Sr urban waters Sr = 0.44 - 4.9 ppm; low Sr urban waters Sr = 0.13 - 0.27 ppm; Fig. 2.6). The rural water compositions have a relatively low range in Ca (85 - 104 ppm) compared to both urban stream and spring water populations, with a somewhat high range of Sr concentrations (0.24 - 2.6 ppm; Fig. 2.6). The dissolution pathway (black line in Fig. 2.6) represents municipal supply water infiltrating and interacting with the Glen Rose limestone, which is the dominant bedrock that Bull Creek watershed streams incise. The range and co-variability of Sr and Ca concentrations in the low Sr urban waters can be accounted for by this dissolution pathway (Fig. 2.6).

Water-rock interaction models that quantify recrystallization (i.e., dissolution and re-precipitation; Fig. 2.7) of calcite and dolomite are used to assess the geochemical processes controlling the stream and spring water composition. Sr/Ca values are highest in the rural and high Sr urban waters (Sr/Ca = 0.001 - 0.013 and 0.001 - 0.018, respectively) with lower overall $^{87}Sr/^{86}Sr$ values (Fig. 2.7A). Rural water $^{87}Sr/^{86}Sr$ values (0.7078-0.7081) are within the range of Cretaceous limestone values (0.7072 - 0.7080; Christian et al., 2011; Koepnick et al., 1985), whereas high Sr urban waters have a larger range (0.7077 - 0.7082; Fig. 2.7A). In contrast to the rural and high Sr urban waters, the low Sr urban waters exhibit relatively low Sr/Ca ratios (0.001 - 0.0005) and high $^{87}Sr/^{86}Sr$ values (0.7082 - 0.7087) compared to the rural and high Sr urban waters (Fig. 2.7A).

The Bull Creek watershed results (Fig. 2.7A) were compared to regional vadose and phreatic groundwater compositions in central Texas (Musgrove et al., 2010; Musgrove and Banner, 2004; Fig. 2.7B) to provide insight to urban water flow pathways. The low Sr urban waters (Fig. 2.7A) are within the range of regional vadose groundwater compositions (Fig. 2.7B). The range of both rural and high Sr urban water compositions (Fig. 2.7A) are within the range measured for regional phreatic groundwater (Fig. 2.7B). Fluids I and II endmembers (Fig. 2.7A and 2.7B) represent values for soil leachates above a central Texas cave (Natural Bridge Cavern; Musgrove and Banner, 2004), which are within the same geologic setting as the present study, and Fluid III (Fig. 2.7A) represents municipal supply water, which has the highest $^{87}Sr/^{86}Sr$ value (present study).

2.5 Discussion

The introduction of treated municipal supply and waste water to the watershed adds complexity to understanding components of the urban hydrologic cycle, especially as impervious cover and municipal water network densities increase with urban growth, and as leakage from municipal water pipes increases with infrastructure age. Numerous studies have relied on physical hydrologic models to estimate the amount of artificial urban recharge (Garcia-Fresca and Sharp, 2005; Sharp, 2010; Bhaskar and Welty, 2012; Passarello et al., 2012; Bhaskar et al., 2016; Minnig et al., 2018), while others have shown discrete geochemical evidence for municipal pipe leakage to groundwater (Barrett et al., 1999; Pu et al, 2014; DeMott, 2006) and baseflow (Christian et al., 2011). Here we focus on geochemical and isotopic tracers to understand how the degree of urban development may influence the geochemical evolution and subsurface flow pathways of municipal water. We address the mechanisms by which artificial recharge (i.e., municipal water leakage and/or irrigation) evolves within the urban hydrologic cycle. This will allow us to understand the alteration of freshwater quantity and quality as urban development continues in the 21st century. That is, the geochemical tools applied in this study can be used to inform the degradation of water quality via waste water leakage that poses risks to sensitive aquatic ecosystems, altered physical groundwater flow pathways, and the quantity of water available to humans and vegetation as urbanization and climate change continues.

2.5.1 Tracing hydrologic endmembers with $^{87}Sr/^{86}Sr$

The distribution of $^{87}Sr/^{86}Sr$ values throughout the Bull Creek watershed can be used to trace the relative influence of contributing water sources (Fig. 2.3). We use the isotopic and elemental differences in endmember waters (e.g., rural and municipal waters) to quantify the effects of urbanization on stream and spring water composition. Our results are consistent with previous studies in the Austin area watersheds where hydrogeologically (and isotopically) distinct endmembers were identified (DeMott, 2006; Christian et al., 2011; Senison et al., 2013). We also address here the previous hypothesis that high $^{87}Sr/^{86}Sr$ values in urban stream and spring water might be caused by natural variability in soil $^{87}Sr/^{86}Sr$ values (Christian et al., 2011).

Unirrigated (i.e., natural) soil $^{87}Sr/^{86}Sr$ values (0.7079-0.7084) cannot account for the range of values observed in the urban stream and spring waters, which range to notably higher values (0.7077 - 0.7095; Fig. 2.3). The range of irrigated soil $^{87}Sr/^{86}Sr$ values (0.7085 - 0.7091), however is distinctly higher than that of unirrigated soils (0.7079–0.7084), with significantly different median values ($p < 0.0001$), and better accounts for the higher $^{87}Sr/^{86}Sr$ values of the urban stream and spring waters (Fig. 2.3). These results discount the natural variability of soils as a source of high $^{87}Sr/^{86}Sr$ to stream and spring waters, and indicates that municipal leakage and/or irrigation water are the dominant contributing sources of waters at urban stream and spring water sites. The higher $^{87}Sr/^{86}Sr$ values of irrigated soil relative to unirrigated soil, and the high irrigated soil values that are similar to municipal water, suggest that soils in the urbanized parts of the watershed evolve toward municipal water $^{87}Sr/^{86}Sr$ values via ion exchange as a consequence of extensive irrigation. That is, high $^{87}Sr/^{86}Sr$ values observed in irrigated soils, and thus the urban stream waters, are a consequence of high $^{87}Sr/^{86}Sr$ values in municipal water.

2.5.2 Controls on urban stream and spring water elemental and isotopic composition

Elevated concentrations of major ions in the urban waters relative to rural waters (Table 1) are indicative of additional endmember contributions (e.g., municipal supply and waste water) to the geochemical composition of the urban waters. Relatively high Na and Cl concentrations are commonly associated with municipal water sources (e.g., Barrett et al., 1999; Leopold, 1968; Porras et al., 2016), which is consistent with the urban waters compositions measured in this study (Table 1; Fig. 2.4). The magnitude by which stream and spring water Na and Cl concentrations are elevated (Fig. 2.4) may be attributed to the degree of urbanization and/or infrastructure age for a sample's subwatershed (Christian et al., 2011). Mixing model results indicate that water from urban water sites consist of approximately 50% - 95% municipal water relative to rural water (Fig. 2.5). In this view, the fluid mixing model underestimates the high Sr urban waters (< 50 % municipal water influence). We show evidence (discussed herein) that the influence of municipal water on the high Sr urban water composition is muted with respect to $^{87}Sr/^{86}Sr$ due to additional geochemical processes. Fluid mixing model results indicates that municipal water infiltration via pipe network leakage and/or irrigation is a significant source of water in the urban hydrologic cycle, even when the watershed is not fully urbanized (e.g., approximately 55% of land is urbanized in the Bull Creek watershed). Our estimates of municipal water influence on urban water composition (50% - 95%) are higher than those estimated by Christian et al. (2011; 40% - 60%) for this watershed. We attribute these differences to the more refined characterization of endmembers at the watershed scale (this study) as opposed to the municipality scale (i.e., seven Austin area watersheds; Christian et al., 2011). Nonetheless, urban water compositions that fall above Fluid Mixing Line I or below Fluid Mixing Line II (Fig. 2.5) (that is, outside the range of modeled compositions) indicate that additional geochemical processes are occurring. The range of municipal waste water compositions (Fig. 2.5) may represent infiltration and exfiltration of soil water and waste water, respectively, within non-watertight infrastructure pipes (e.g., Goebel et al., 2004; Endreny and Collins, 2009).

2.5.3 Delineating geochemical processes and flow pathways

The introduction of municipal water into the natural soil-limestone system induces new water-rock interaction processes, whereby infiltrated municipal water can geochemically interact with the limestone host rock. We propose that the geochemical interactions of infiltrating municipal water evolves via diagnostic patterns, which can be used to delineate relative groundwater residence times (Musgrove and Banner, 2004; Wong et al., 2014). The low Sr urban water have relatively high concentrations of Ca relative to Sr and lie directly along the modeled limestone dissolution pathway from the municipal endmember (Fig. 2.6). The low Sr urban water also has relatively low Sr/Ca values (Fig. 2.7A), which are associated with vadose zone to mixed phreatic-vadose zone (i.e., shallow) flow and short to intermediate groundwater residence times (i.e., low water-rock interaction; Fig. 2.7B). The vadose zone waters in Fig. 2.7B were analyzed from regional cave dripwaters (Musgrove et al., 2010; Musgrove and Banner, 2004) and represent infiltrated rainwater through the unsaturated (vadose) zone. Mixed phreatic-vadose zone groundwaters were sampled from springs (Fig. 2.7A, B), which are active when the groundwater table is sufficiently high, but geochemical evidence suggests that less evolved water (i.e., vadose zone) influences these spring water compositions (Musgrove and Banner, 2004; Wong et al., 2014). Both the rural and high Sr urban waters have higher Sr/Ca values and lower $^{87}Sr/^{86}Sr$ values than the low Sr urban water (Fig. 2.7A) and vadose zone water (Fig. 2.7B). Moreover, the rural and high Sr urban water $^{87}Sr/^{86}Sr$ values are relatively low, within the range of Cretaceous limestone (0.7072 - 0.7080, Christian et al., 2001; Koepnick et al., 1985). The water-rock interaction results for the rural and high Sr urban waters (Fig. 2.7A) indicate that these waters have relatively long groundwater residence times, similar to regional phreatic groundwater compositions (Fig. 2.7B). We note that the variability in the high Sr urban waters is larger than those observed in the rural waters, which is likely due to the evolution process of municipal water (relatively high $^{87}Sr/^{86}Sr$) interacting with the carbonate bedrock (relatively low $^{87}Sr/^{86}Sr$). Our water-rock interaction model results (Fig. 2.7A) are consistent with geochemical evolution models developed from regional phreatic and vadose groundwater in central Texas (Fig. 2.7B; Musgrove et al., 2010; Musgrove and Banner, 2004; Wong et al., 2014). We infer that the geochemical evolution observed in the urban stream and spring waters (both high and low Sr waters) reflects changes in the physical flow pathways as municipal water infiltrates as vadose zone flow (high $^{87}Sr/^{86}Sr$ and low Sr/Ca in low Sr urban waters; Fig. 2.7A, B) to phreatic flow (low $^{87}Sr/^{86}Sr$ and high Sr/Ca in high Sr urban waters; Fig. 2.7A, B).

2.5.4 Conceptual framework for the urban hydrologic cycle

Studies that document natural groundwater flow pathways in central Texas show that recharge may take shallow (i.e., vadose zone), or deep (i.e., phreatic zone), or mixed flow pathways (e.g., Smith et al., 2015; Musgrove et al., 2015; Musgrove and Banner, 2014), depending on antecedent moisture conditions and the density of carbonate dissolution features (e.g., Wong et al., 2012). Urban development, however, complicates the controls on these flow pathways due to the alteration of both surface (e.g., impervious cover) and subsurface (e.g., municipal pipe networks) characteristics. We present a conceptual framework to illustrate the altered flow pathways between a rural (Fig. 2.8A) and urban (Fig. 2.8B) setting. Our geochemical modeling results, compared to regional results that reflect rural settings (e.g. Musgrove et al., 2015; Musgrove and Banner, 2014), indicate varying groundwater residence times for Bull Creek stream and spring waters. Our urban stream and spring water results show geochemical evidence for varying flow pathways followed by municipal leakage and/or irrigation water, which are distinct and include: 1) shallow vadose zone flow (low Sr urban waters, hollow red arrow in Fig. 2.8B) and 2) deep phreatic groundwater flow (high Sr urban waters, solid red arrow in Fig. 2.8B). Extensive groundwater residence times and water-rock interaction can account for water compositions at both rural and high Sr urban water (Fig. 2.7A), whereas the low Sr urban water has compositions consistent with lower extents of water-rock interaction and shorter groundwater residence times (Fig. 2.7A). The low Sr urban water has compositions that can be accounted for by limestone dissolution (0.5 - 2 mmol/L; Fig. 2.6), as opposed to recrystallization (which would yield relatively higher Sr concentrations; Fig. 2.6). We infer that limestone dissolution occurs as municipal water interacts with the limestone host rock along vadose zone flow paths. This conceptual framework (Fig. 2.8) is based on geochemical evidence (Fig. 2.7). Here we show increased municipal to rural fluid mixing (approximately 50% - 95%) within the low Sr urban waters (hollow red line in Fig. 2.8B) relative to the rural waters (blue lines in Fig. 2.8B). In this case, shallow municipal leakage geochemically dominates via artificial recharge. This may occur through one or both of two processes: 1) a high volume of municipal water mutes the geochemical signature of naturally infiltrating precipitation or 2) dense impervious cover limits the amount of naturally infiltrating precipitation and artificial recharge dominates the shallow groundwater system. Moreover, the municipal geochemical signature within the urban phreatic groundwater system (e.g., high Sr urban waters; Fig 8A) may evolve toward natural water geochemical compositions due to long groundwater residence time and/or the volume of natural phreatic groundwater with which the municipal water mixes. Based on observation well data (n = 2) in the Bull Creek watershed, the groundwater table fluctuates between 15 to 20 meters below ground surface. This concept is consistent with the findings of Musgrove et al. (2010), who demonstrate the geochemical evolution of natural water as residence time and the extent of water-rock interaction increases. That is, vadose zone flow is the least geochemically evolved, phreatic groundwater is the most evolved, and spring discharge represents a mixture between vadose zone and phreatic groundwater (Fig. 2.7B).

2.5.5 Implications

Our results provide a quantitative framework for understanding how municipal water impacts natural water geochemical compositions and interacts with the hydrologic cycle as a function of urbanization. Physical hydrologic modeling that previously estimated the volume of artificial recharge (e.g., Garcia-Fresca and Sharp, 2005; Sharp, 2010; Bhaskar and Welty, 2012; Passarello et al., 2012; Bhaskar et al., 2016; Minnig et al., 2018) may be advanced by estimates of relative extents and groundwater residences times of municipal water. This identification of the evolution of municipal water as it enters limestone bedrock will bear on the growing understanding of the complexities of the urban hydrologic cycle. We propose that this geochemical modeling approach can be applied across watersheds with varying degrees of urban development (e.g., Fig 1) to quantify regional alterations to the urban hydrologic cycle, especially cities with isotopically distinct municipal and natural groundwater and stream water sources (e.g., Chesson et al., 2015). These conditions are satisfied in many United States cities (Chesson et al., 2015), including St. Louis, Missouri, which supplies municipal water from the Mississippi and Missouri Rivers ($^{87}Sr/^{86}Sr$ = 0.7095 and 0.7010, respectively; Goldstein and Jacobsen, 1987; Christian et al., 2011) to the city that is built upon Paleozoic marine carbonate rocks ($^{87}Sr/^{86}Sr$ = 0.7085; Christian et al., 2011). Spokane, Washington, delivers municipal water from Lake Missoula ($^{87}Sr/^{86}Sr$ = 0.7183; Bataille and Bowen, 2012), which is distinct from the city's underlying Columbia River Basalts ($^{87}Sr/^{86}Sr$ = 0.7320; Chesson et al., 2015). We expect that many cities worldwide exhibit isotopic distinctions between watershed geology and municipal water (e.g., Chesson et al., 2015 for U.S. cities). Thus, the integrated use of the geochemical and isotopic tools presented herein may have wide application to delineate the impacts of urbanization on the hydrologic cycle.

Continued research to quantify urbanization impacts may bolster how we manage freshwater resources in the 21st century and may reveal both advantages and disadvantages of such impacts on the urban hydrologic cycle. That is, infiltrated municipal water (via leakage and/or irrigation) quantified in this study may provide consistent water availability for vegetation and sensitive aquatic ecosystems, especially under the increased frequency of drought conditions projected for central Texas in the 21st century (Hayhoe, 2014; Swain and Hayhoe, 2015). The Lower Colorado River Authority manages water supplies for both the city of Austin and Gulf Coast rice growing operations, but only the city's municipal water supply is guaranteed (Lower Colorado River Authority, 2015). When reservoir levels persisted at just 30% from 2011-2015, the water provisioned to Gulf Coast rice growing operations was interrupted (2012-2015) and city irrigation was curtailed (2009-present) to mitigate against decreases in Austin's municipal water supply (Breyer et al., 2018; Lower Colorado River Authority, 2015). In watersheds where irrigation practices persisted, the watershed-scale drought severity decreased, resulting in increased resiliency of urban vegetation and stream flow (Breyer et al., 2018). The contribution of city's municipal supply water to watersheds via water main leakage and/or irrigation demonstrated in the present study, however, may significantly affect the long-term availability and energy costs of both municipal and agricultural water supplies. Moreover, our estimations of groundwater residence times and the delineated physical flow pathways of infiltrating municipal water can be projected toward waste water and raw effluent leakage, which likely take these same physical flow pathways and pose contamination risks to watersheds and underlying aquifers.

2.6 Conclusions

The spatial variability of elemental and isotopic ($^{87}Sr/^{86}Sr$) compositions in stream and spring water samples in a rapidly urbanizing carbonate watershed in central Texas was assessed to delineate the influence of municipal (supply and waste); the watershed exhibits a pronounced urbanization gradient, with parts that are rural and parts that are highly developed. We show that $^{87}Sr/^{86}Sr$ is a robust geochemical tool to trace the influence of municipal water on natural water geochemical composition, facilitated by the distribution of distinct endmember $^{87}Sr/^{86}Sr$ values in this hydrogeologic setting. Distinctly higher exchangable $^{87}Sr/^{86}Sr$ values for irrigated soils relative to unirrigated soils suggests that municipal water resets soil compositions over time, and that municipal water (via pipe network leakage and/or irrigation) is the source of high $^{87}Sr/^{86}Sr$ values observed in streams, springs, and irrigated soils. A marked increase in waste water constituent (Na and Cl) concentrations was observed among many of the urban stream and spring water samples, but Na and Cl concentrations remained relatively low in the rural waters, indicating that municipal waste water affects the urban stream and spring water composition.

Quantification of municipal water influence on stream and spring water composition demonstrates that municipal water can be a significant source of recharge, even when the watershed is semi-urbanized. That is, urban stream and spring water compositions in the Bull Creek watershed (approximately 55% urbanized) are influenced by significant fluid mixing with municipal water (up to 95%). Water-rock interaction modeling constrains geochemical processes induced by the introduction of infiltrating municipal water into the limestone host rock. Water-rock interaction models are diagnostic for identifying relative groundwater residence times among groundwater samples, and are used to delineate flow pathways within the urban hydrologic cycle. To gain this perspective, Bull Creek watershed stream and spring water geochemical compositions are compared to those of regional groundwater (e.g., phreatic and vadose zone). These results indicate that infiltrated municipal water may have both short (i.e., vadose zone) or long (i.e. phreatic zone) residence times prior to stream or spring discharge.

2.7 Acknowledgements

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2.8 Figures and Tables

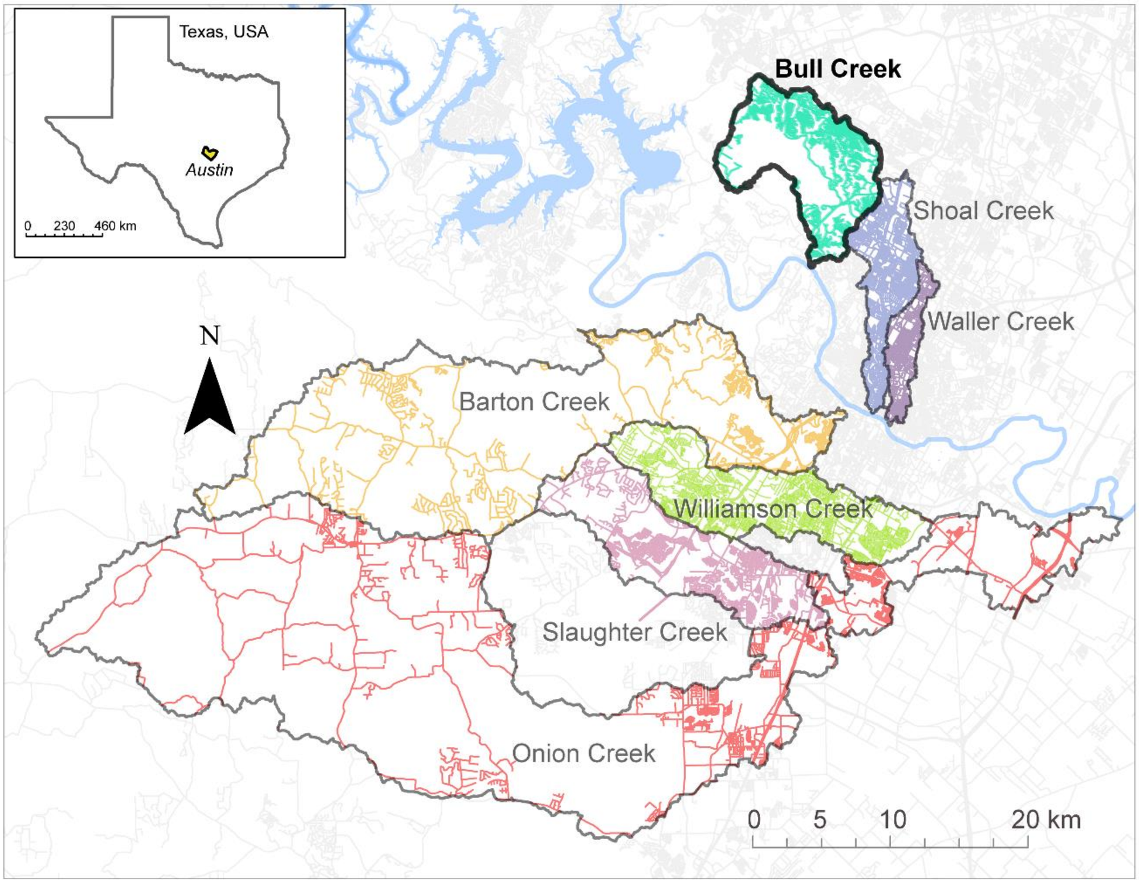

Figure 2.1 Regional map of Austin area watersheds showing road densities (multi-colored lines). Bull Creek watershed is outlined with thick black line. Modified from Christian et al. (2011).

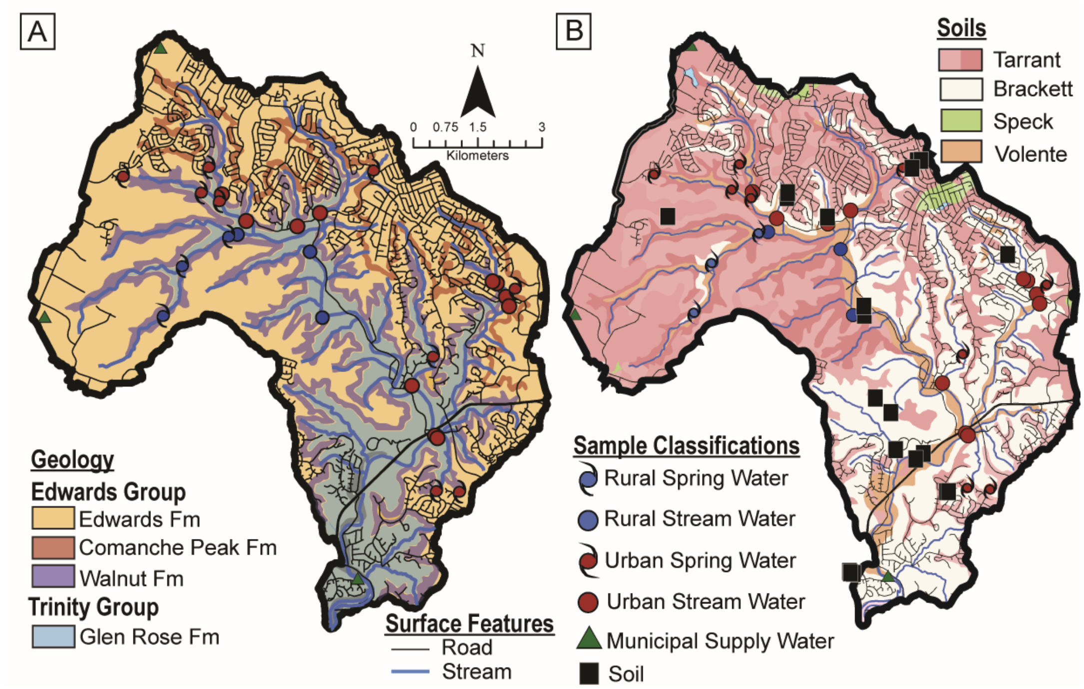

Figure 2.2 Map of Bull Creek watershed showing sampled rural and urban stream water sites (red and blue, respectively). (A) Shows the geologic units within the watershed, and (B) shows distribution of four dominant soils. Geologic data was obtained from the Bureau of Economic Geology, The University of Texas at Austin (Geology of the Austin area; 1:62,500 scale). Soil data was obtained from the USDA NRCS Geospatial Data Gateway.

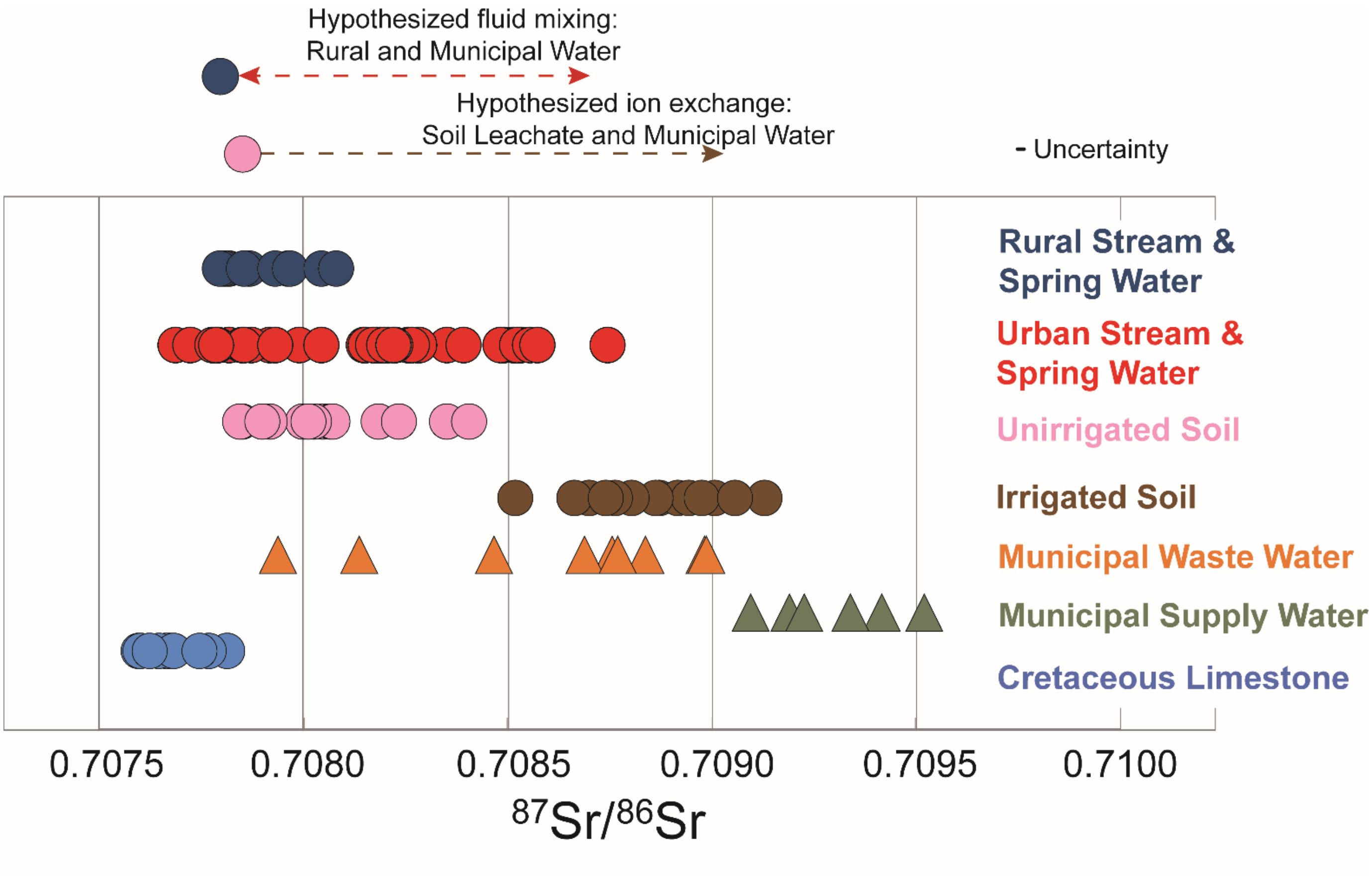

Figure 2.3 Distribution of $^{87}Sr/^{86}Sr$ values for Bull Creek stream and spring water, soils, municipal (supply and waste) water, and Cretaceous limestone in Bull Creek watershed. Hypothesized geochemical processes (dashed arrows) are inferred for the evolution of water and soils from starting compositions (circles at start of dashed arrows).

Table 2.1 Range of geochemical concentrations (mg/L) and $^{87}Sr/^{86}Sr$ values for the measured waters. BDL indicates measurements below detection limit.

	High Sr Urban	**Low Sr Urban**	**Rural**	**Municipal Supply**	**Municipal Waste**
mg/L	Range *(standard deviation)*				
Ca	75 - 146 *(21.3)*	67 - 166 *(28.6)*	85 - 104 *(5.4)*	11 - 12 *(0.5)*	15 - 37 *(6.6)*
Mg	16 - 29 *(3.6)*	11 - 33 *(4.9)*	16 - 26 *(3.3)*	14 - 18 *(1.5)*	16 - 21 *(2.0)*
Na	15 - 74 *(17.7)*	11 - 41 *(7.1)*	7 - 11 *(1.0)*	18 - 31 *(4.9)*	43 - 105 *(19.2)*
K	0.4 - 4 (1.0)	0.9 - 4.4 (0.9)	0.5 - 1.3 *(0.3)*	3.2 - 4.9 (0.6)	BDL - 26 *(7.0)*
NO_3	0.3 - 16.6 *(4.5)*	0.8 - 28.7 *(8.0)*	BDL - 3.5 *(1.2)*	0.5 - 2 *(0.6)*	BDL - 2.1 *(0.7)*
SO_4	20 - 128 *(30.8)*	17 - 71 *(13.5)*	15 - 32 *(5.6)*	22 - 32 (3.3)	32 - 120 (26.4)
Cl	28 - 93 *(22.0)*	19 - 88 *(16.0)*	16 - 26 *(3.0)*	27 - 44 *(7.1)*	57 - 167 *(33.5)*
Sr	0.44 - 4.90 *(1.4)*	0.30 - 0.27 *(0.04)*	0.24 - 2.60 *(0.7)*	0.11 - 0.13 *(0.01)*	0.12 - 0.40 *(0.1)*
HCO_3	250-481 *(62.7)*	245-468 *(64.6)*	308-359 *(17.7)*	60-76 *(6.3)*	94-166 *(24.0)*
$^{87}Sr/^{86}Sr$	0.7077-0.7082 *(0.0002)*	0.7082-0.7087 *(0.0002)*	0.7078-0.7081 *(0.0001)*	0.7091-0.7095 *(0.0001)*	0.7079-0.7090 *(0.0004)*

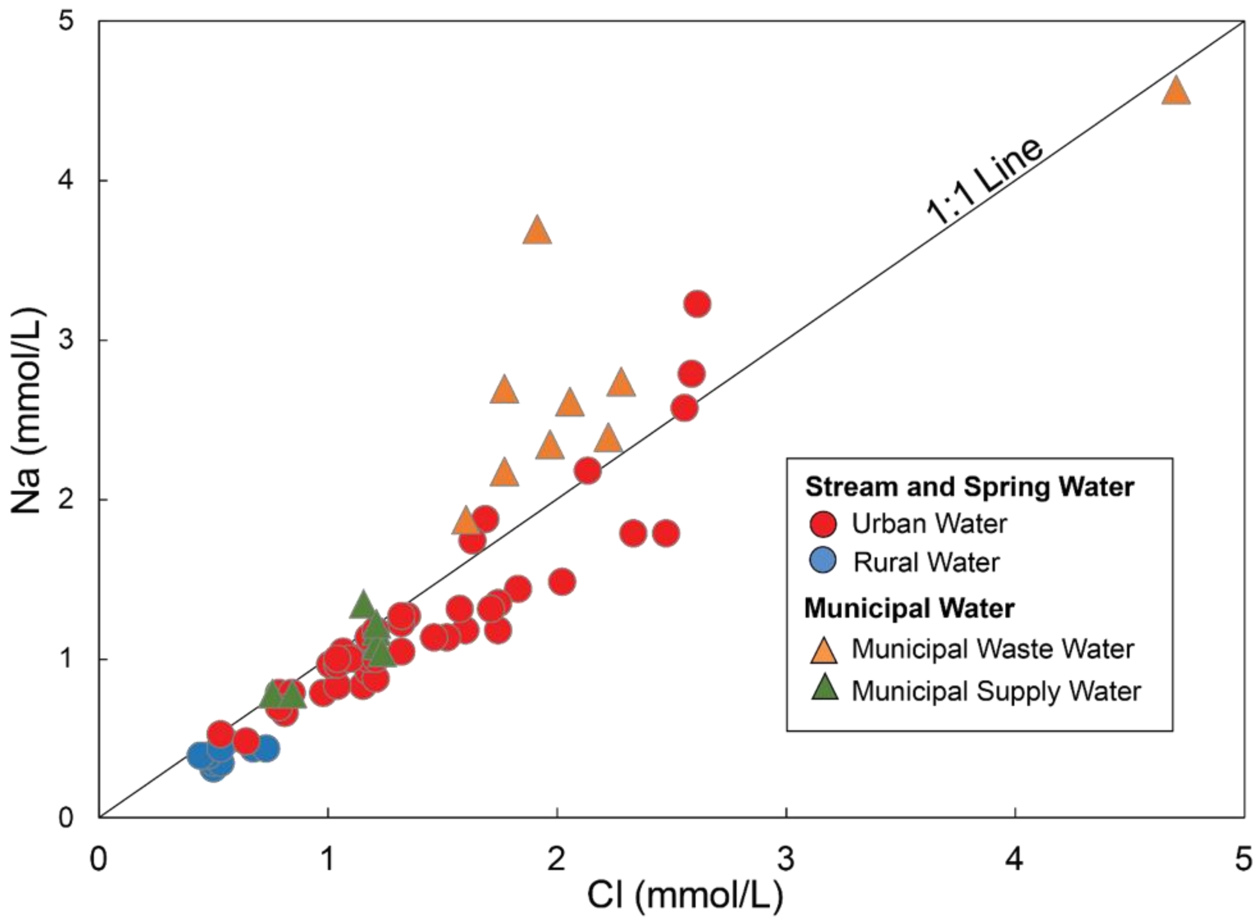

Figure 2.4 Cl and Na (mmol/L) variations for municipal supply (green triangles) and waste (orange triangles) water, rural stream and spring water (blue circles), and urban stream and spring water (red circles). Line shows the 1:1 molar ratio of Cl : Na concentrations.

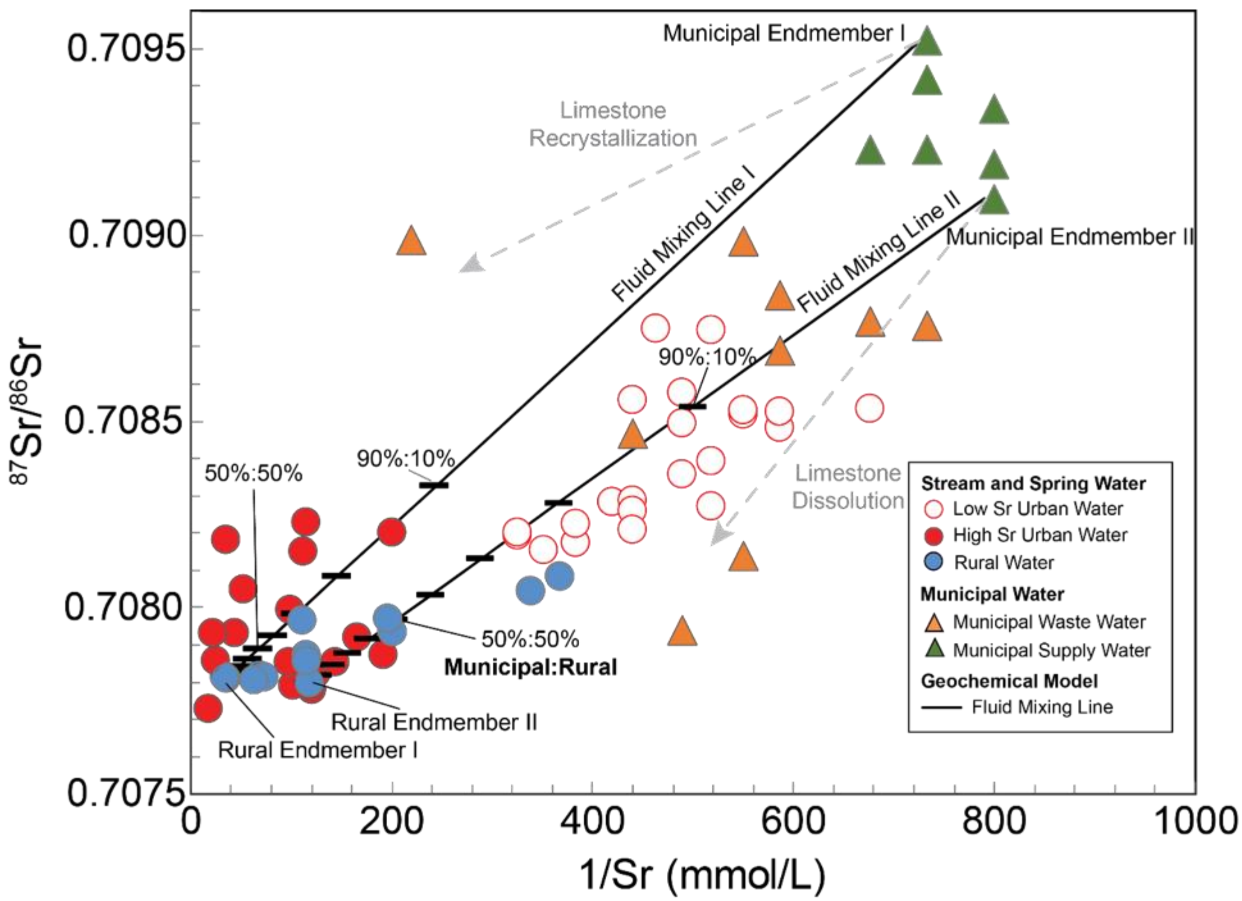

Figure 2.5 Geochemical model illustrating fluid mixing between rural and municipal supply water. Fluid Mixing Line I shows mixing between Rural Endmember I (1/Sr=35.7, $^{87}Sr/^{86}Sr$=0.7078) and Municipal Endmember I (1/Sr=735.3, $^{87}Sr/^{86}Sr$=0.7095). Fluid Mixing Line II shows mixing between Rural Endmember II (1/Sr=117.6, 87Sr/86Sr=0.7078) and Municipal Endmember II (1/Sr=800.0, $^{87}Sr/^{86}Sr$=0.7091). Each tick represents a 10% change in the proportion of municipal water in the modeled fluid mixture. The fluid mixing model indicates that some low-Sr urban waters consist of up to 95% municipal water. Grey dashed lines depict inferred geochemical processes including limestone recrystallization or dissolution.

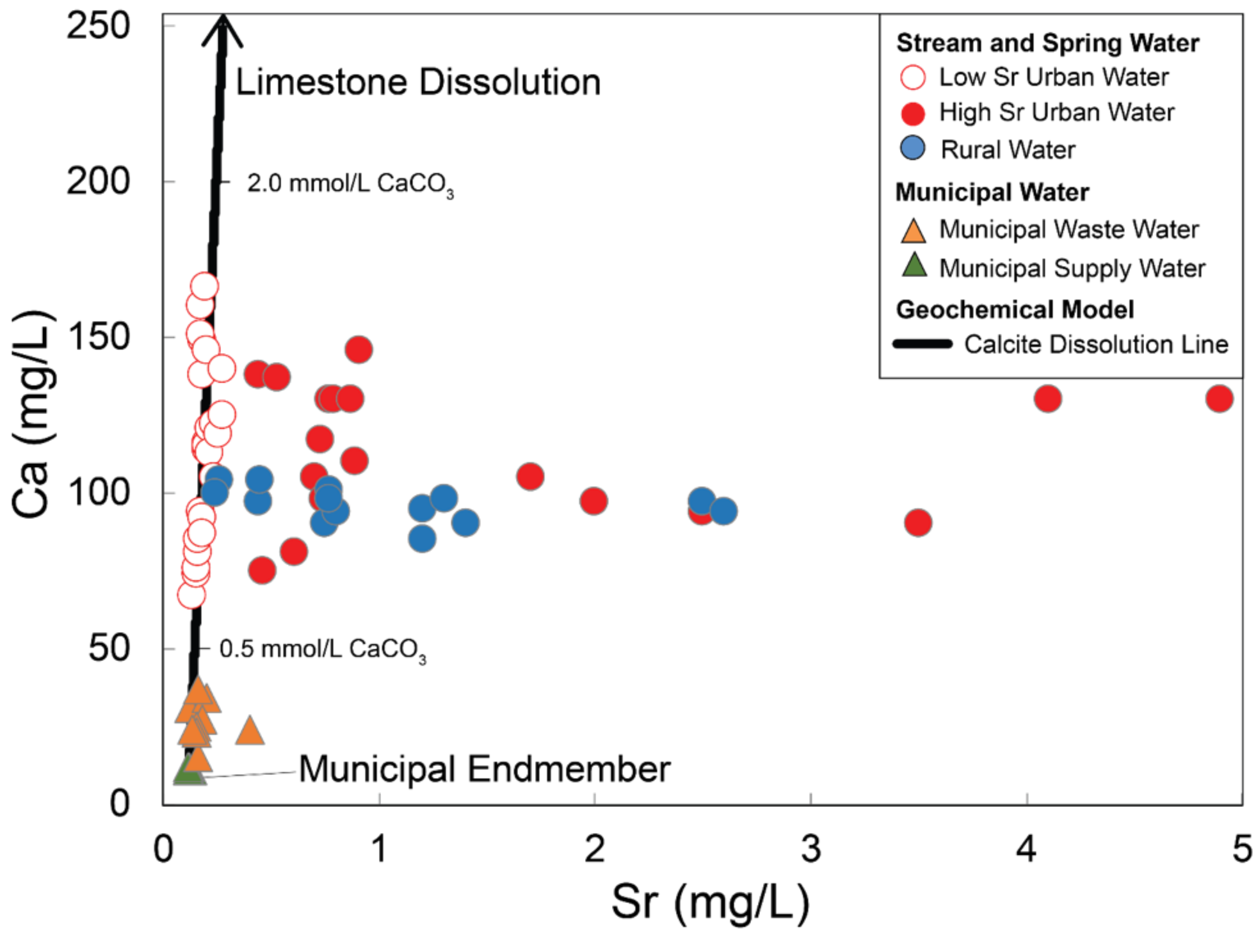

Figure 2.6 Geochemical model for dissolution (black arrow) of the Glen Rose Limestone by interaction with municipal supply water (green triangles). Numbers along the dissolution line represent the amount of limestone dissolved into solution (in units of mmol/L). Measured municipal supply and waste water (green and orange triangles, respectively) and low Sr urban stream and spring waters (hollow red circles) plot along this line, while the rural (blue circles) and high Sr urban (solid red circles) stream and spring waters exhibit an increased Sr concentration relative to Ca.

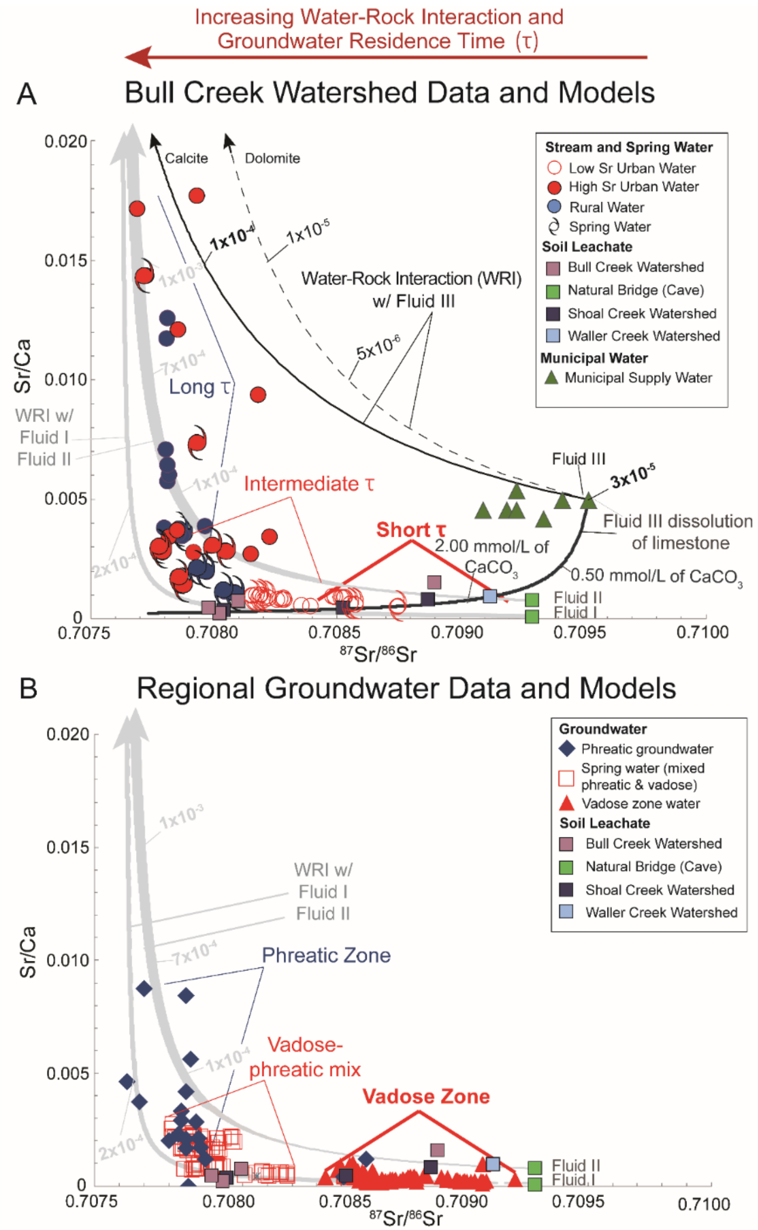

Fig 2.7 $^{87}Sr/^{86}Sr$ values vs Sr/Ca molar ratios for (A) Bull Creek and soil leachates, and (B) regional phreatic, spring, vadose zone groundwater from Musgrove et al. (2010), and soil leachates. Short, Intermediate, and Long τ (in A) indicate relative groundwater residence times. Modeled water-rock interaction (WRI) curves shows the evolution of initial fluids (I, II, & III) through progressive increases in recrystallization (i.e., dissolution and re-precipitation) of calcite and dolomite. That is, modeled WRI III curve (in A) shows the incremental increase in Sr/Ca and decrease in $^{87}Sr/^{86}Sr$ values as Fluid III (municipal supply water) undergoes increased water-rock interaction with calcite (solid black line) and dolomite (dashed black line). Modeled WRI I & II curves (grey) represent the range (i.e., widths) of recrystallization for calcite and dolomite starting at Fluids I & II, respectively. Arrows indicate increase in water-rock molar values for each modeled curve (incremental amounts of calcite and dolomite reported along each curve in mmol/L). Fluids I and II are the range of soil leachates presented in Musgrove et al. (2010), and were sampled above a central Texas cave (Natural Bridge Caverns, located about 70 miles south-southwest of Austin). Fluid III (in A) is the measured municipal supply water sample (this study) with greatest $^{87}Sr/^{86}Sr$ value (0.7095).

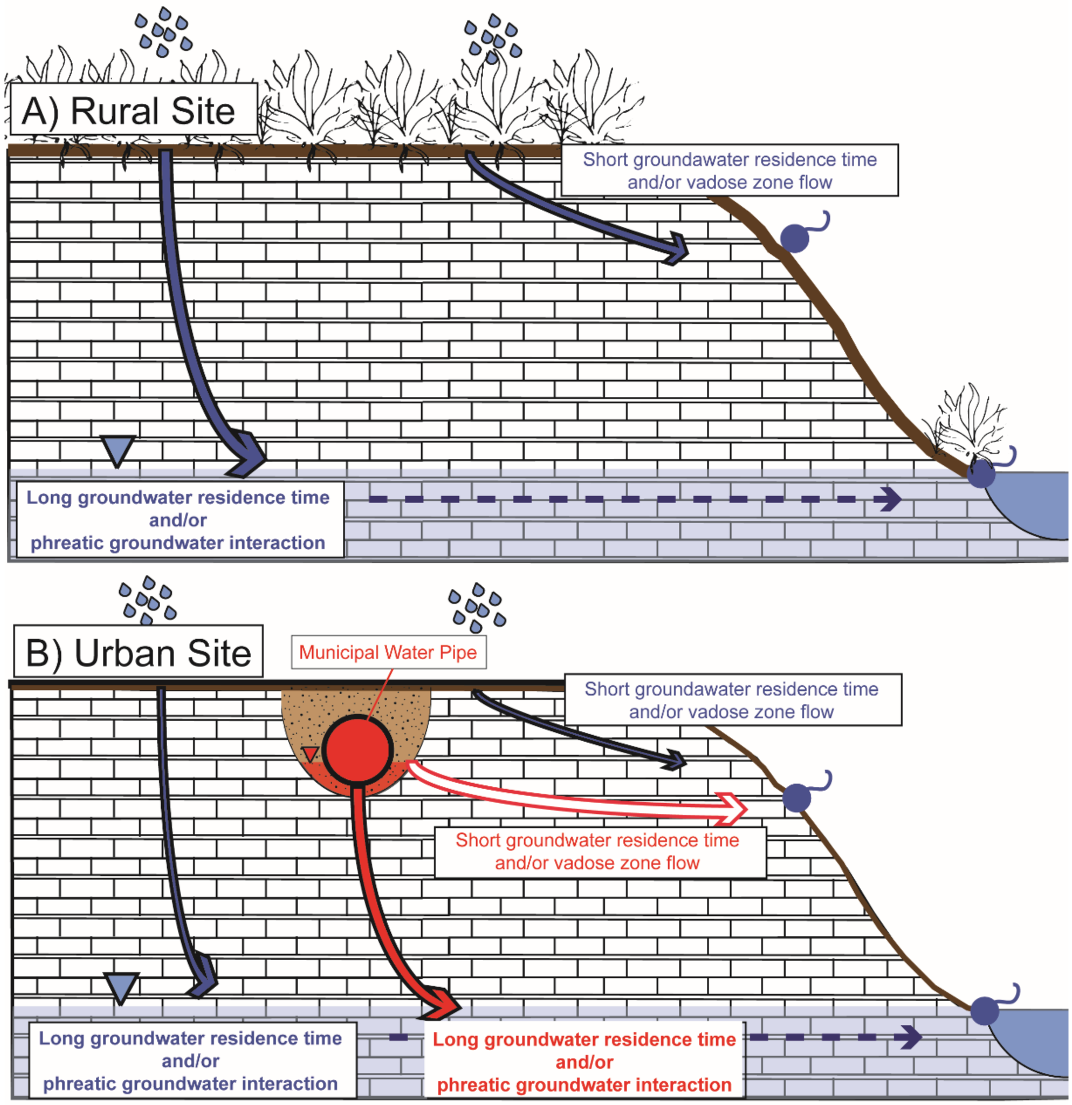

Fig 2.8 Conceptual model of hypothesized flow paths for rural (blue arrows) and municipal water (red arrows), from recharge to spring discharge (blue circles). (A) Rural site: Depicts rural water flow pathways (phreatic and vadose zone). (B) Urban site: Depicts altered surface characteristics (e.g., unvegetated surface with impervious cover) and subsurface flow paths. Flow paths of municipal (supply water) leakage originate at the gravel packed trench and include 1) shallow flow with low residence time (hollow red arrow; i.e., vadose zone flow), and 2) deep flow with high residence time (solid red arrow; i.e., phreatic flow). Rural water originates from precipitation (in A and B) and is hypothesized to contribute to both phreatic and vadose zone flow. The contribution of infiltrating precipitation is inferred to be less in the urban site schematic (B) (depicted by relatively smaller blue arrows than for the rural site schematic (A)).

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Concluding Statement

This thesis documents geochemical evidence of hydrogeologic processes within two contrasting carbonate aquifers, both of which have been subject to anthropogenic and hydroclimatic stresses in past decades. Although the research objectives, impacts, hydrologic settings, and climates vary between the two aquifers, common geochemical tools are used to assess local hydrologic sources and processes, which can inform future management of freshwater resources. Water movement through carbonate aquifers is complex, and the geochemical tools used in this thesis document the value of coupling physical and chemical data to constrain flow paths. The results of water-rock interaction and fluid-mixing models in this thesis document the controls on groundwater composition in both a tropical (Chapter I) and a sub-tropical (Chapter II) carbonate aquifer, but the extent to which these processes contribute to the groundwater (or surface water in Bull Creek, Chapter II) compositions is variable both within and between the two studies. In the Guam carbonate aquifer (Chapter I), variability in the subsurface geology and the presence/absence of underlying seawater controls whether water-rock interaction or fluid mixing between freshwater and seawater influence the groundwater composition. These results are consistent with the existing conceptual model, which was heretofore based on physical observations and modeling. In the Bull Creek watershed (Chapter II), differences between water-rock interaction and fluid-mixing processes that constrain the urban spring and stream water geochemical compositions are likely a function of flow path as municipal water infiltrates through the subsurface. That is, we hypothesize that shallow, conduit, flow pathways of municipal water explain one urban water group, whereas deep flow pathways (conduit and diffuse) of municipal water and/or interaction with phreatic groundwater accounts for the other urban water group. Results from Chapter II provide a geochemical technique to quantify groundwater residence times and infer flow paths of municipal water within the urban hydrologic cycle.

This thesis highlights the vulnerability of carbonate aquifers to anthropogenic alterations of freshwater quantity and quality, and results from each study can be used to inform future management practices. That is, the documented timing and modes of recharge to Guam's aquifer (Chapter I), in conjunction with projected decreases in future freshwater (via increase pumpage and decrease rainfall amount), can inform how the island will plan for freshwater supply changes in the coming decades. In Bull Creek (Chapter II), the results provide a quantitative framework for understanding how municipal water impacts natural water quality and affects the hydrologic cycle. Results can be helpful to mitigate impacts related to urban development practices including the loss of municipal water via water-main leakage and/or irrigation, which may significantly decrease the available freshwater supplies and increase energy needs to clean and deliver more water. The impacts highlighted in this thesis may become exacerbated with local to global population growth and continuing climate change.

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Appendix I (Chapter I) Supplementary Material

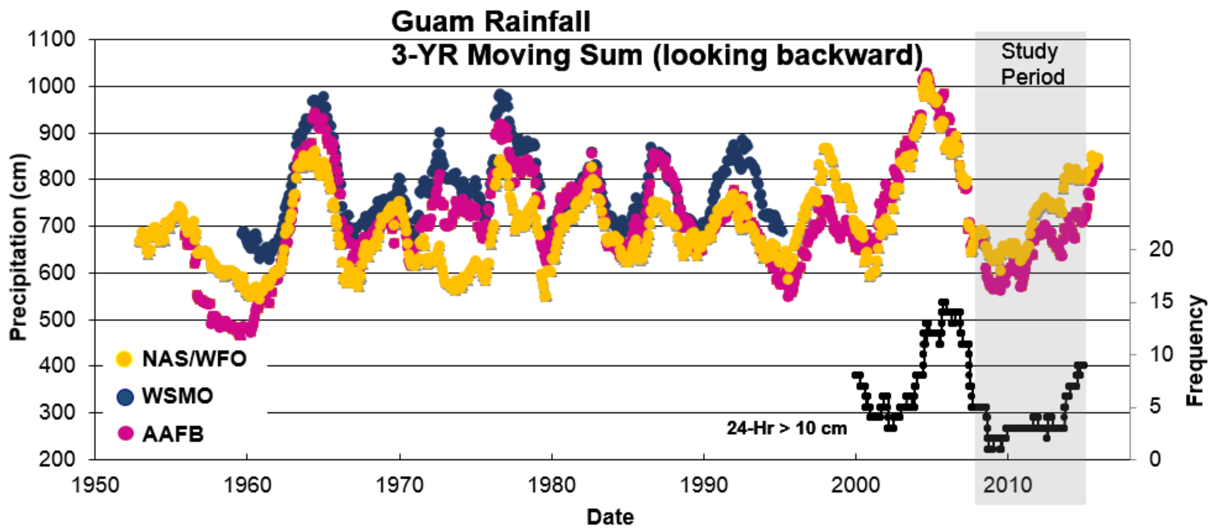

Figure S1.1 3-year moving sum of precipitation recorded at three Guam climate sites: the Guam Naval Air Station/Weather Forecast Office (NAS/WFO); the NOAA Weather Service Meteorological Observatory (WSMO), and Andersen Air Force Base (AAFB). Note the climate context of the cave study period (shaded) shows a steady and substantial (250 cm per 5-years) increase of rainfall from a very dry beginning to a wet finish. The substantial increase of total rainfall was also accompanied by a substantial increase in the number of days with heavy (>10 cm in 24 hours) rainfall. Inset (black) shows occurrences of 3-year moving sum where rainfall was >10 cm.

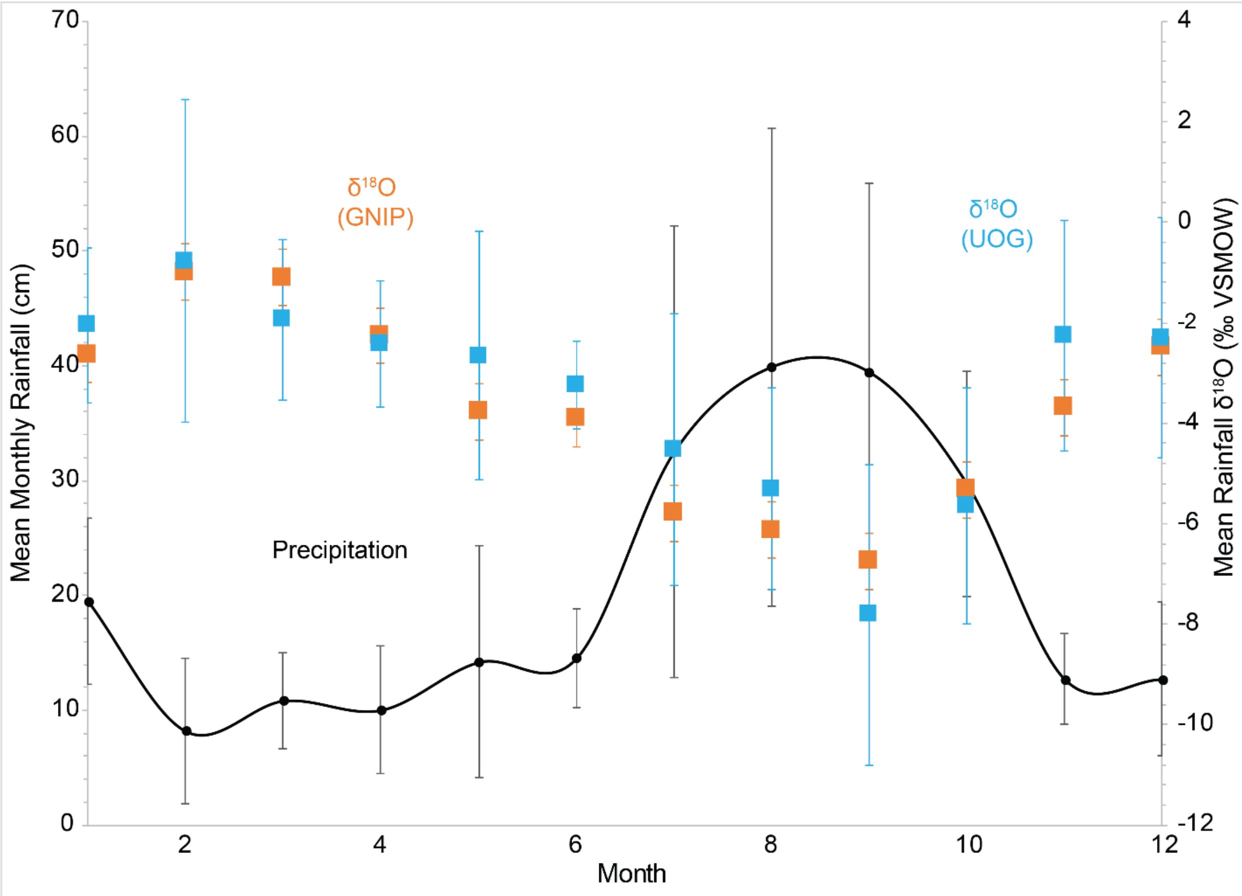

Figure S1.2 Average monthly rainfall (2008-2015) and $\delta^{18}O$ values for northern Guam measured at the University of Guam (UOG; 2008-2015) and retrieved from the Global Network of Isotopes in Precipitation (GNIP; 1961-67 and 1973-77). Error bars show standard deviation.

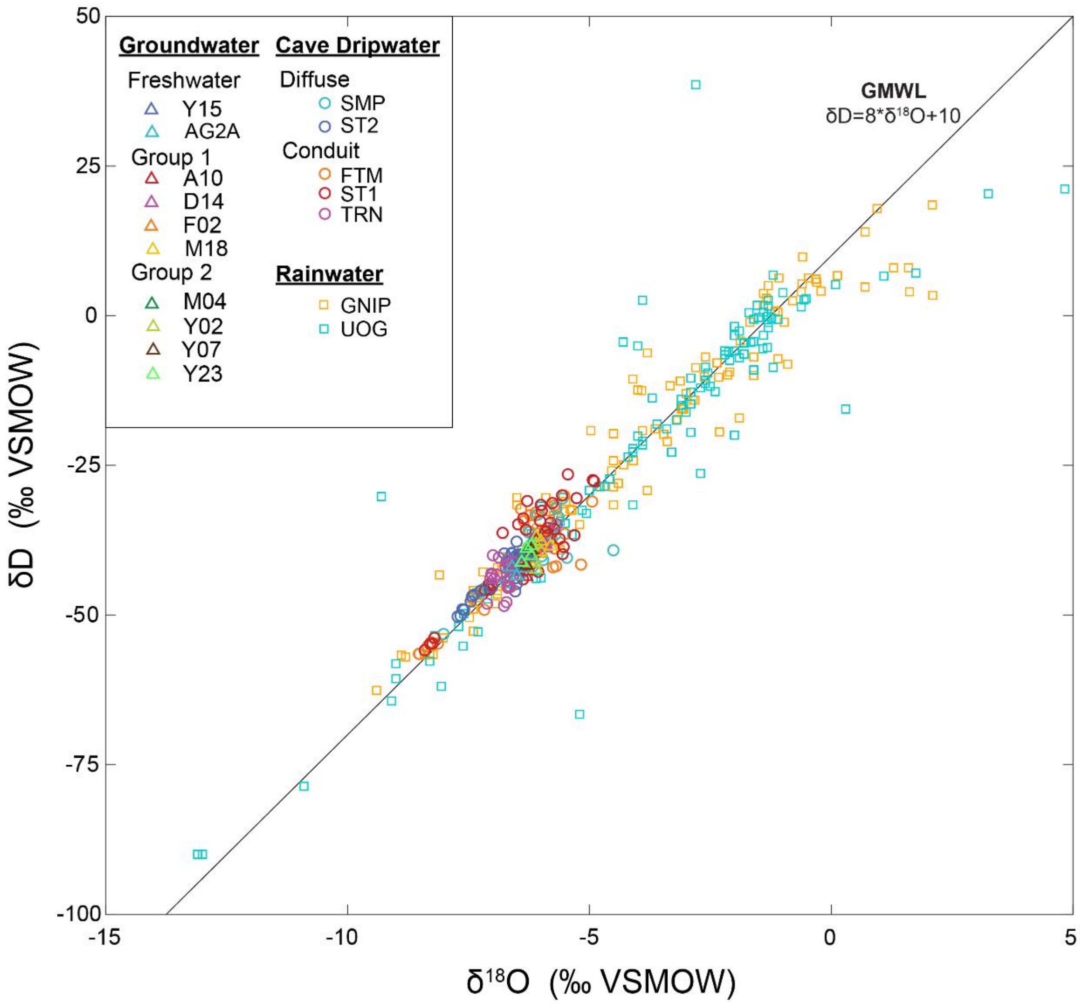

Figure S1.3 Northern Guam rainfall, cave dripwater, and groundwater δD and δ^{18}O values relative to the global meteoric water line (GMWL).

Table S1. El Niño Southern Oscillation (ENSO) indices over study period (2008-2015), spanning El Niño (red), La Niña (blue), and neutral ENSO (black)

Year	DJF	JFM	FMA	MAM	AMJ	MJJ	JJA	JAS	ASO	SON	OND	NDJ
2008	**-1.6**	**-1.4**	**-1.2**	**-0.9**	**-0.8**	**-0.5**	-0.4	-0.3	-0.3	-0.4	**-0.6**	**-0.7**
2009	**-0.8**	**-0.7**	**-0.5**	-0.2	0.1	0.4	**0.5**	**0.5**	**0.7**	**1.0**	**1.3**	**1.6**
2010	**1.5**	**1.3**	**0.9**	0.4	-0.1	**-0.6**	**-1.0**	**-1.4**	**-1.6**	**-1.7**	**-1.7**	**-1.6**
2011	**-1.4**	**-1.1**	**-0.8**	**-0.6**	**-0.5**	-0.4	**-0.5**	**-0.7**	**-0.9**	**-1.1**	**-1.1**	**-1.0**
2012	**-0.8**	**-0.6**	**-0.5**	-0.4	-0.2	0.1	0.3	0.3	0.3	0.2	0.0	-0.2
2013	-0.4	-0.3	-0.2	-0.2	-0.3	-0.3	-0.4	-0.4	-0.3	-0.2	-0.2	-0.3
2014	-0.4	-0.4	-0.2	0.1	0.3	0.2	0.1	0.0	0.2	0.4	**0.6**	**0.7**
2015	**0.6**	**0.6**	**0.6**	**0.8**	**1.0**	**1.2**	**1.5**	**1.8**	**2.1**	**2.4**	**2.5**	**2.6**

Data from Rayner et al. (2003).

Table S1.2 Cave dripwater and groundwater cation concentrations

Sample Date [a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
9/23/2008	FTM*	Dripwater	76.9	11.2	28.2	0.2	ALPS
9/23/2008	FTM*	Dripwater	84.6	11.8	29.2	0.2	ALPS
9/23/2008	FTM*	Dripwater	85.0	11.9	29.2	0.2	ALPS
10/21/2008	FTM*	Dripwater	74.7	10.7	36.2	0.2	ALPS
10/21/2008	FTM*	Dripwater	79.4	11.5	39.3	0.2	ALPS
11/18/2008	FTM*	Dripwater	71.6	11.6	35.9	0.2	ALPS
11/18/2008	FTM*	Dripwater	77.0	12.1	37.6	0.2	ALPS
11/18/2008	FTM*	Dripwater	76.8	12.3	36.7	0.2	ALPS
12/16/2008	FTM*	Dripwater	79.0	11.0	34.6	0.2	ALPS
12/16/2008	FTM*	Dripwater	79.3	11.3	36.5	0.2	ALPS
12/16/2008	FTM*	Dripwater	82.7	11.8	37.2	0.2	ALPS
1/13/2009	FTM*	Dripwater	70.9	11.2	35.6	0.2	ALPS
1/13/2009	FTM*	Dripwater	75.6	11.9	38.0	0.2	ALPS
2/18/2009	FTM*	Dripwater	68.8	13.8	88.4	0.2	ALPS
2/18/2009	FTM*	Dripwater	70.8	11.2	36.0	0.2	ALPS
2/18/2009	FTM*	Dripwater	76.9	12.0	37.8	0.2	ALPS
3/17/2009	FTM*	Dripwater	65.4	11.6	74.7	0.2	ALPS
3/17/2009	FTM*	Dripwater	73.5	11.9	38.5	0.2	ALPS
4/14/2009	FTM*	Dripwater	67.7	11.8	76.2	0.2	DGS Q ICP-MS
4/14/2009	FTM*	Dripwater	70.9	11.3	36.4	0.2	DGS Q ICP-MS
5/13/2009	FTM*	Dripwater	81.4	11.9	39.3	0.2	ALPS
5/13/2009	FTM*	Dripwater	83.0	11.9	38.8	0.2	ALPS
5/13/2009	FTM*	Dripwater	83.3	12.0	39.1	0.2	ALPS
6/12/2009	FTM*	Dripwater	81.3	12.7	44.3	0.2	ALPS
6/12/2009	FTM*	Dripwater	82.6	11.7	38.0	0.2	ALPS
6/12/2009	FTM*	Dripwater	82.3	11.7	38.0	0.2	ALPS
6/12/2009	FTM*	Dripwater	85.4	11.7	38.4	0.2	ALPS
7/15/2009	FTM*	Dripwater	79.4	10.9	38.3	0.2	ALPS
7/15/2009	FTM*	Dripwater	86.2	11.8	39.5	0.2	ALPS
7/15/2009	FTM*	Dripwater	85.6	11.9	38.6	0.2	ALPS
8/22/2009	FTM*	Dripwater	80.2	10.8	38.6	0.2	DGS Q ICP-MS
8/22/2009	FTM*	Dripwater	81.1	10.9	37.7	0.2	DGS Q ICP-MS
9/22/2009	FTM*	Dripwater	75.1	10.6	36.3	0.2	ALPS
9/22/2009	FTM*	Dripwater	77.7	11.1	35.2	0.2	ALPS
9/22/2009	FTM*	Dripwater	79.2	11.4	35.2	0.2	ALPS

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Sample Date[a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
10/21/2009	FTM*	Dripwater	80.3	10.9	38.2	0.2	DGS Q ICP-MS
10/21/2009	FTM*	Dripwater	78.7	10.7	36.6	0.2	DGS Q ICP-MS
11/24/2009	FTM	Dripwater	80.1	10.9	37.3	0.2	DGS Q ICP-MS
12/22/2009	FTM	Dripwater	80.1	11.2	35.9	0.2	DGS Q ICP-MS
1/26/2010	FTM	Dripwater	73.2	11.2	36.1	0.2	DGS Q ICP-MS
3/2/2010	FTM	Dripwater	78.1	11.0	36.4	0.2	DGS Q ICP-MS
4/6/2010	FTM	Dripwater	80.6	10.9	37.5	0.2	DGS Q ICP-MS
5/4/2010	FTM	Dripwater	77.4	10.8	37.1	0.2	DGS Q ICP-MS
6/8/2010	FTM	Dripwater	79.4	10.8	37.1	0.2	DGS Q ICP-MS
7/13/2010	FTM	Dripwater	73.1	10.6	37.9	0.2	DGS Q ICP-MS
8/17/2010	FTM	Dripwater	79.5	10.8	38.5	0.2	DGS Q ICP-MS
9/28/2010	FTM*	Dripwater	82.0	8.0	28.5	0.2	ALPS
9/28/2010	FTM*	Dripwater	86.9	8.6	29.3	0.2	ALPS
10/26/2010	FTM	Dripwater	80.2	10.9	39.7	0.2	DGS Q ICP-MS
11/23/2010	FTM	Dripwater	79.2	11.2	37.3	0.2	ALPS
12/21/2010	FTM	Dripwater	77.5	11.2	36.3	0.2	DGS Q ICP-MS
1/25/2011	FTM	Dripwater	75.9	11.6	35.8	0.2	ALPS
2/22/2011	FTM	Dripwater	74.7	11.8	33.5	0.2	DGS Q ICP-MS
4/26/2011	FTM	Dripwater	78.1	12.3	30.3	0.2	ALPS
5/24/2011	FTM	Dripwater	74.3	11.9	29.5	0.2	ALPS
6/21/2011	FTM	Dripwater	70.4	11.9	30.7	0.2	ALPS
7/19/2011	FTM	Dripwater	76.9	12.2	32.2	0.2	ALPS
8/30/2011	FTM*	Dripwater	48.9	12.4	29.5	0.2	ALPS
8/30/2011	FTM*	Dripwater	73.3	12.0	28.8	0.2	ALPS
9/27/2011	FTM	Dripwater	86.7	12.7	33.2	0.2	ALPS
10/25/2011	FTM	Dripwater	84.4	12.8	34.4	0.2	ALPS
11/22/2011	FTM	Dripwater	86.2	12.7	35.1	0.2	ALPS
12/20/2011	FTM	Dripwater	82.0	12.5	34.2	0.2	ALPS
1/24/2012	FTM	Dripwater	81.3	11.0	36.2	0.2	ALPS
2/28/2012	FTM	Dripwater	76.1	11.4	33.9	0.2	DGS Q ICP-MS
3/27/2012	FTM	Dripwater	72.6	11.1	33.3	0.2	DGS Q ICP-MS
4/23/2012	FTM	Dripwater	70.8	11.0	33.2	0.2	DGS Q ICP-MS
5/22/2012	FTM	Dripwater	72.5	11.2	34.2	0.2	DGS Q ICP-MS
6/29/2012	FTM	Dripwater	79.4	11.2	34.8	0.2	DGS Q ICP-MS
7/31/2012	FTM	Dripwater	83.5	11.6	36.1	0.2	DGS Q ICP-MS
8/28/2012	FTM	Dripwater	76.7	11.2	34.9	0.2	DGS Q ICP-MS
9/25/2012	FTM	Dripwater	75.9	11.0	28.6	0.2	DGS Q ICP-MS

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Sample Date [a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
10/23/2012	FTM	Dripwater	73.9	11.7	26.5	0.2	DGS Q ICP-MS
11/20/2012	FTM	Dripwater	74.0	11.3	24.7	0.2	DGS Q ICP-MS
12/22/2012	FTM	Dripwater	74.1	11.2	26.5	0.2	DGS Q ICP-MS
1/16/2013	FTM	Dripwater	76.0	11.5	28.6	0.2	DGS Q ICP-MS
3/19/2013	FTM	Dripwater	72.8	11.1	28.3	0.2	DGS Q ICP-MS
4/23/2013	FTM	Dripwater	77.4	11.1	28.9	0.2	DGS Q ICP-MS
5/21/2013	FTM	Dripwater	75.9	11.0	28.8	0.2	DGS Q ICP-MS
6/26/2013	FTM	Dripwater	76.0	11.0	29.2	0.2	DGS Q ICP-MS
7/30/2013	FTM	Dripwater	80.7	11.0	30.0	0.2	DGS Q ICP-MS
8/27/2013	FTM	Dripwater	79.7	11.2	29.7	0.2	DGS Q ICP-MS
9/24/2013	FTM	Dripwater	79.1	10.3	30.8	0.2	DGS Q ICP-MS
10/22/2013	FTM	Dripwater	81.7	10.5	32.9	0.2	DGS Q ICP-MS
11/19/2013	FTM	Dripwater	79.9	10.5	31.3	0.2	DGS Q ICP-MS
12/17/2013	FTM	Dripwater	75.4	10.8	31.7	0.2	DGS Q ICP-MS
9/23/2008	SMP	Dripwater	62.9	11.2	110.1	0.2	ALPS
10/21/2008	SMP*	Dripwater	70.0	10.1	48.3	0.2	ALPS
10/21/2008	SMP*	Dripwater	74.1	10.9	52.4	0.2	ALPS
11/18/2008	SMP	Dripwater	58.6	9.8	91.8	0.2	ALPS
12/16/2008	SMP	Dripwater	53.9	11.3	104.2	0.2	ALPS
1/13/2009	SMP	Dripwater	55.5	11.5	106.8	0.2	ALPS
2/18/2009	SMP*	Dripwater	61.5	10.5	51.0	0.2	DGS Q ICP-MS
2/18/2009	SMP*	Dripwater	62.2	10.9	52.1	0.2	DGS Q ICP-MS
3/17/2009	SMP*	Dripwater	62.4	10.9	50.1	0.2	ALPS
3/17/2009	SMP*	Dripwater	62.9	10.4	50.1	0.2	ALPS
3/17/2009	SMP*	Dripwater	65.7	11.4	51.8	0.2	ALPS
4/14/2009	SMP*	Dripwater	68.5	10.2	49.0	0.2	ALPS
4/14/2009	SMP*	Dripwater	65.9	11.0	52.1	0.2	ALPS
4/14/2009	SMP*	Dripwater	66.2	11.3	51.2	0.2	ALPS
5/13/2009	SMP	Dripwater	59.2	10.7	52.6	0.2	ALPS
6/12/2009	SMP*	Dripwater	70.9	10.5	50.6	0.2	ALPS
6/12/2009	SMP*	Dripwater	71.5	11.0	51.4	0.2	ALPS
6/12/2009	SMP*	Dripwater	75.7	11.2	52.0	0.2	ALPS
7/15/2009	SMP*	Dripwater	69.2	10.4	49.7	0.2	ALPS
7/15/2009	SMP*	Dripwater	68.8	10.6	49.2	0.2	ALPS
8/22/2009	SMP*	Dripwater	78.2	10.4	50.3	0.2	ALPS
8/22/2009	SMP*	Dripwater	83.0	11.1	51.7	0.2	ALPS
8/22/2009	SMP*	Dripwater	83.4	11.1	50.9	0.2	ALPS

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Sample Date [a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
9/22/2009	SMP*	Dripwater	79.8	10.5	50.5	0.2	ALPS
9/22/2009	SMP*	Dripwater	78.4	10.6	49.0	0.2	ALPS
10/21/2009	SMP*	Dripwater	73.2	10.4	49.0	0.2	ALPS
10/21/2009	SMP*	Dripwater	77.2	11.0	50.1	0.2	ALPS
10/21/2009	SMP*	Dripwater	77.0	11.0	49.1	0.2	ALPS
11/24/2009	SMP	Dripwater	69.3	10.6	46.3	0.2	ALPS
12/22/2009	SMP	Dripwater	44.9	9.6	43.5	0.1	DGS Q ICP-MS
1/26/2010	SMP	Dripwater	65.3	11.0	45.8	0.2	ALPS
3/2/2010	SMP	Dripwater	46.5	9.8	44.0	0.1	DGS Q ICP-MS
4/6/2010	SMP	Dripwater	42.5	10.5	48.3	0.1	DGS Q ICP-MS
5/4/2010	SMP	Dripwater	52.7	9.6	46.1	0.1	DGS Q ICP-MS
6/8/2010	SMP	Dripwater	56.3	10.2	47.6	0.1	DGS Q ICP-MS
8/17/2010	SMP	Dripwater	64.8	10.6	47.3	0.2	ALPS
9/28/2010	SMP	Dripwater	41.1	9.5	49.3	0.1	DGS Q ICP-MS
11/22/2010	SMP	Dripwater	47.1	9.8	36.1	0.1	DGS Q ICP-MS
12/21/2010	SMP	Dripwater	65.8	10.8	47.8	0.2	ALPS
2/22/2011	SMP	Dripwater	63.2	11.1	47.0	0.2	ALPS
9/27/2011	SMP	Dripwater	75.2	11.1	43.5	0.2	ALPS
4/23/2012	SMP	Dripwater	60.2	10.4	44.3	0.1	DGS Q ICP-MS
5/22/2012	SMP	Dripwater	51.2	9.8	42.7	0.1	DGS Q ICP-MS
8/28/2012	SMP	Dripwater	58.9	10.2	43.9	0.2	DGS Q ICP-MS
9/25/2012	SMP	Dripwater	71.7	10.1	42.1	0.1	DGS Q ICP-MS
10/23/2012	SMP	Dripwater	67.5	10.1	42.2	0.1	DGS Q ICP-MS
11/20/2012	SMP	Dripwater	56.9	9.8	41.8	0.1	DGS Q ICP-MS
12/22/2012	SMP	Dripwater	60.4	10.1	40.9	0.1	DGS Q ICP-MS
2/19/2013	SMP	Dripwater	47.7	9.7	40.3	0.1	DGS Q ICP-MS
3/19/2013	SMP*	Dripwater	66.4	9.0	22.2	0.1	DGS Q ICP-MS
3/19/2013	SMP*	Dripwater	64.2	8.6	20.8	0.1	DGS Q ICP-MS
3/19/2013	SMP*	Dripwater	73.0	10.4	35.9	0.1	DGS Q ICP-MS
3/19/2013	SMP*	Dripwater	69.0	10.2	34.6	0.1	DGS Q ICP-MS
3/19/2013	SMP*	Dripwater	71.8	10.2	34.4	0.1	DGS Q ICP-MS
3/19/2013	SMP*	Dripwater	69.0	10.2	40.3	0.1	DGS Q ICP-MS
4/23/2013	SMP*	Dripwater	70.2	9.7	40.5	0.1	DGS Q ICP-MS
4/23/2013	SMP*	Dripwater	72.5	9.8	39.9	0.1	DGS Q ICP-MS
5/21/2013	SMP	Dripwater	73.4	9.9	39.5	0.1	DGS Q ICP-MS
6/26/2013	SMP	Dripwater	75.8	10.0	39.7	0.1	DGS Q ICP-MS
6/29/2013	SMP	Dripwater	45.7	9.7	40.8	0.1	DGS Q ICP-MS

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Sample Date [a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
7/30/2013	SMP	Dripwater	76.4	9.9	39.5	0.1	DGS Q ICP-MS
8/27/2013	SMP	Dripwater	75.9	9.8	39.1	0.1	DGS Q ICP-MS
9/24/2013	SMP	Dripwater	44.3	9.5	39.3	0.1	DGS Q ICP-MS
10/22/2013	SMP	Dripwater	39.6	4.1	19.8	0.1	DGS Q ICP-MS
11/19/2013	SMP	Dripwater	73.8	9.7	39.4	0.1	DGS Q ICP-MS
12/17/2013	SMP	Dripwater	69.3	9.8	39.5	0.1	DGS Q ICP-MS
1/21/2014	SMP	Dripwater	57.4	9.8	39.4	0.1	DGS Q ICP-MS
2/17/2014	SMP	Dripwater	72.2	9.7	38.8	0.1	DGS Q ICP-MS
3/18/2014	SMP	Dripwater	70.7	9.6	38.5	0.1	DGS Q ICP-MS
4/23/2014	SMP	Dripwater	73.2	9.8	39.1	0.1	DGS Q ICP-MS
5/23/2014	SMP	Dripwater	73.2	9.7	38.7	0.1	DGS Q ICP-MS
6/17/2014	SMP	Dripwater	74.0	9.6	38.3	0.1	DGS Q ICP-MS
8/18/2014	SMP	Dripwater	72.4	9.4	37.2	0.1	DGS Q ICP-MS
9/23/2014	SMP	Dripwater	72.4	9.5	37.3	0.1	DGS Q ICP-MS
10/31/2014	SMP	Dripwater	56.0	9.4	37.4	0.1	DGS Q ICP-MS
11/29/2014	SMP*	Dripwater	47.9	9.3	36.7	0.1	DGS Q ICP-MS
11/29/2014	SMP*	Dripwater	71.0	9.4	36.3	0.1	DGS Q ICP-MS
12/30/2014	SMP	Dripwater	48.7	9.3	36.8	0.1	DGS Q ICP-MS
1/31/2015	SMP	Dripwater	48.5	9.3	36.9	0.1	DGS Q ICP-MS
2/28/2015	SMP	Dripwater	58.3	9.3	36.2	0.1	DGS Q ICP-MS
3/28/2015	SMP	Dripwater	63.9	9.6	37.5	0.2	DGS Q ICP-MS
5/2/2015	SMP	Dripwater	59.9	9.3	35.9	0.1	DGS Q ICP-MS
5/30/2015	SMP	Dripwater	66.7	9.5	36.3	0.1	DGS Q ICP-MS
6/26/2015	SMP	Dripwater	62.5	9.3	35.1	0.1	DGS Q ICP-MS
7/30/2015	SMP	Dripwater	73.4	9.5	35.3	0.1	DGS Q ICP-MS
9/1/2015	SMP	Dripwater	70.8	9.0	33.4	0.1	DGS Q ICP-MS
9/29/2015	SMP	Dripwater	69.5	8.9	32.2	0.1	DGS Q ICP-MS
10/27/2015	SMP	Dripwater	69.7	8.9	31.9	0.1	DGS Q ICP-MS
12/29/2015	SMP	Dripwater	48.3	8.8	31.4	0.1	DGS Q ICP-MS
1/24/2008	ST1	Dripwater	49.9	11.4	41.4	0.2	DGS Q ICP-MS
2/8/2008	ST1	Dripwater	48.9	11.1	40.5	0.2	DGS Q ICP-MS
2/29/2008	ST1	Dripwater	42.6	11.2	41.1	0.1	DGS Q ICP-MS
3/7/2008	ST1	Dripwater	30.3	10.8	39.9	0.1	DGS Q ICP-MS
3/14/2008	ST1	Dripwater	37.5	11.4	42.0	0.1	DGS Q ICP-MS
5/27/2008	ST1	Dripwater	48.7	11.4	43.1	0.2	DGS Q ICP-MS
7/21/2008	ST1	Dripwater	45.9	11.2	42.7	0.2	DGS Q ICP-MS
8/15/2008	ST1	Dripwater	59.9	10.2	37.8	0.2	DGS Q ICP-MS

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Sample Date[a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
9/23/2008	ST1*	Dripwater	52.1	10.3	33.2	0.2	ALPS
9/23/2008	ST1*	Dripwater	53.8	10.6	34.4	0.2	ALPS
10/21/2008	ST1*	Dripwater	56.7	10.1	34.5	0.2	DGS Q ICP-MS
10/21/2008	ST1*	Dripwater	56.9	10.6	36.0	0.2	DGS Q ICP-MS
11/18/2008	ST1*	Dripwater	52.4	10.0	35.0	0.2	ALPS
11/18/2008	ST1*	Dripwater	54.2	10.7	37.3	0.2	ALPS
12/16/2008	ST1*	Dripwater	46.4	9.8	34.9	0.2	ALPS
12/16/2008	ST1*	Dripwater	46.9	10.3	36.9	0.1	ALPS
12/16/2008	ST1*	Dripwater	48.9	10.9	37.2	0.2	ALPS
1/13/2009	ST1*	Dripwater	33.2	10.0	37.7	0.2	ALPS
1/13/2009	ST1*	Dripwater	34.5	10.5	38.4	0.1	ALPS
1/13/2009	ST1*	Dripwater	35.8	10.5	37.9	0.1	ALPS
2/18/2009	ST1*	Dripwater	36.0	10.0	38.6	0.1	ALPS
2/18/2009	ST1*	Dripwater	36.2	10.7	39.0	0.1	ALPS
2/18/2009	ST1*	Dripwater	37.4	10.8	38.9	0.2	ALPS
4/14/2009	ST1*	Dripwater	44.4	10.2	39.0	0.1	DGS Q ICP-MS
4/14/2009	ST1*	Dripwater	45.8	10.1	39.1	0.1	DGS Q ICP-MS
5/13/2009	ST1*	Dripwater	51.9	10.2	40.1	0.2	ALPS
5/13/2009	ST1*	Dripwater	52.7	10.9	40.6	0.2	ALPS
5/13/2009	ST1*	Dripwater	51.8	10.7	39.4	0.2	ALPS
6/12/2009	ST1*	Dripwater	44.9	10.1	40.0	0.2	ALPS
6/12/2009	ST1*	Dripwater	45.7	10.9	41.0	0.2	ALPS
6/12/2009	ST1*	Dripwater	46.3	10.9	41.0	0.2	ALPS
7/15/2009	ST1*	Dripwater	41.2	10.3	40.9	0.1	ALPS
7/15/2009	ST1*	Dripwater	41.4	10.5	40.6	0.1	ALPS
8/22/2009	ST1*	Dripwater	67.7	9.8	37.0	0.1	DGS Q ICP-MS
8/22/2009	ST1*	Dripwater	66.7	9.9	35.2	0.2	DGS Q ICP-MS
9/22/2009	ST1*	Dripwater	67.4	9.3	31.0	0.1	ALPS
9/22/2009	ST1*	Dripwater	71.9	9.9	31.1	0.2	ALPS
9/22/2009	ST1*	Dripwater	72.9	10.0	30.9	0.2	ALPS
10/21/2009	ST1*	Dripwater	58.1	9.8	34.8	0.1	DGS Q ICP-MS
10/21/2009	ST1*	Dripwater	58.4	9.9	33.8	0.1	DGS Q ICP-MS
11/24/2009	ST1	Dripwater	56.9	10.1	33.0	0.1	DGS Q ICP-MS
12/22/2009	ST1	Dripwater	54.8	10.2	31.9	0.1	DGS Q ICP-MS
1/26/2010	ST1	Dripwater	55.3	10.5	32.8	0.1	DGS Q ICP-MS
3/2/2010	ST1	Dripwater	48.7	10.5	33.5	0.1	DGS Q ICP-MS
5/4/2010	ST1	Dripwater	36.3	10.0	35.6	0.1	DGS Q ICP-MS

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Sample Date [a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
6/8/2010	ST1	Dripwater	42.0	10.2	36.3	0.1	DGS Q ICP-MS
7/13/2010	ST1	Dripwater	39.4	10.1	36.5	0.1	DGS Q ICP-MS
8/17/2010	ST1	Dripwater	41.9	10.2	36.5	0.1	DGS Q ICP-MS
9/28/2010	ST1	Dripwater	34.5	10.2	38.2	0.1	DGS Q ICP-MS
10/26/2010	ST1	Dripwater	60.2	10.0	34.2	0.2	DGS Q ICP-MS
11/23/2010	ST1	Dripwater	62.2	10.9	34.9	0.2	ALPS
12/21/2010	ST1	Dripwater	52.5	10.9	36.4	0.2	ALPS
1/25/2011	ST1	Dripwater	32.6	10.0	34.6	0.1	ALPS
2/22/2011	ST1	Dripwater	57.1	9.7	31.3	0.2	ALPS
3/29/2011	ST1	Dripwater	51.3	10.6	35.5	0.1	DGS Q ICP-MS
4/26/2011	ST1	Dripwater	77.6	10.9	39.4	0.2	ALPS
5/24/2011	ST1	Dripwater	52.4	10.6	34.1	0.1	ALPS
6/21/2011	ST1	Dripwater	46.2	10.6	36.3	0.2	ALPS
7/19/2011	ST1	Dripwater	49.5	10.7	37.2	0.2	ALPS
8/30/2011	ST1	Dripwater	75.0	10.5	31.1	0.2	ALPS
9/27/2011	ST1	Dripwater	73.0	9.6	28.7	0.2	ALPS
10/25/2011	ST1	Dripwater	55.1	10.3	29.3	0.2	ALPS
11/22/2011	ST1	Dripwater	46.3	9.7	24.0	0.1	ALPS
12/20/2011	ST1	Dripwater	50.4	10.5	28.4	0.1	ALPS
1/24/2012	ST1	Dripwater	52.1	10.9	31.0	0.2	ALPS
2/28/2012	ST1	Dripwater	42.2	9.9	29.6	0.1	ALPS
3/27/2012	ST1	Dripwater	28.5	10.2	33.4	0.1	ALPS
5/22/2012	ST1	Dripwater	36.5	9.9	33.4	0.1	ALPS
7/31/2012	ST1	Dripwater	36.5	10.4	36.0	0.1	ALPS
8/28/2012	ST1	Dripwater	58.7	9.1	25.7	0.1	ALPS
9/25/2012	ST1	Dripwater	63.0	9.8	28.0	0.1	ALPS
10/23/2012	ST1	Dripwater	55.0	9.1	23.6	0.1	ALPS
11/20/2012	ST1	Dripwater	46.3	9.9	31.4	0.1	ALPS
12/22/2012	ST1	Dripwater	37.3	9.5	29.6	0.1	ALPS
3/19/2013	ST1	Dripwater	27.5	9.6	32.6	0.1	ALPS
5/21/2013	ST1	Dripwater	29.1	9.7	33.5	0.1	ALPS
6/26/2013	ST1	Dripwater	30.7	10.3	35.5	0.1	ALPS
7/30/2013	ST1	Dripwater	52.3	10.1	34.3	0.1	ALPS
9/24/2013	ST1	Dripwater	58.5	9.2	26.5	0.1	ALPS
10/22/2013	ST1	Dripwater	64.5	8.2	23.4	0.1	ALPS
11/19/2013	ST1	Dripwater	54.6	9.1	26.1	0.1	ALPS
12/17/2013	ST1	Dripwater	40.6	9.3	27.8	0.1	ALPS

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Sample Date [a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
1/21/2014	ST1	Dripwater	29.1	9.2	29.6	0.1	ALPS
2/17/2014	ST1	Dripwater	39.1	9.4	25.5	0.1	ALPS
3/18/2014	ST1	Dripwater	37.2	9.4	27.8	0.1	ALPS
6/17/2014	ST1	Dripwater	56.2	9.7	30.5	0.1	ALPS
8/18/2014	ST1	Dripwater	57.5	9.1	24.8	0.1	ALPS
10/31/2014	ST1	Dripwater	57.9	8.9	20.2	0.1	DGS Q ICP-MS
11/29/2014	ST1	Dripwater	46.6	8.9	22.9	0.1	DGS Q ICP-MS
12/30/2014	ST1	Dripwater	35.1	9.3	25.4	0.1	DGS Q ICP-MS
1/31/2015	ST1	Dripwater	48.6	9.4	21.8	0.1	DGS Q ICP-MS
3/28/2015	ST1*	Dripwater	35.4	9.5	25.5	0.1	DGS Q ICP-MS
3/28/2015	ST1*	Dripwater	72.1	10.0	33.9	0.1	DGS Q ICP-MS
3/28/2015	ST1*	Dripwater	76.4	10.1	34.4	0.1	DGS Q ICP-MS
9/23/2008	ST2*	Dripwater	79.4	10.6	43.1	0.2	DGS Q ICP-MS
9/23/2008	ST2*	Dripwater	80.3	10.8	44.0	0.2	DGS Q ICP-MS
10/21/2008	ST2*	Dripwater	72.6	10.6	42.2	0.2	ALPS
10/21/2008	ST2*	Dripwater	33.2	11.5	46.3	0.2	ALPS
11/18/2008	ST2*	Dripwater	78.2	10.4	41.7	0.2	ALPS
11/18/2008	ST2*	Dripwater	82.3	11.2	44.5	0.2	ALPS
12/16/2008	ST2*	Dripwater	76.6	10.4	40.7	0.2	ALPS
12/16/2008	ST2*	Dripwater	82.9	11.2	44.8	0.2	ALPS
1/13/2009	ST2*	Dripwater	77.7	10.4	40.4	0.2	DGS Q ICP-MS
1/13/2009	ST2*	Dripwater	80.4	10.9	43.1	0.2	DGS Q ICP-MS
2/18/2009	ST2*	Dripwater	77.9	10.3	41.9	0.2	ALPS
2/18/2009	ST2*	Dripwater	79.3	11.1	43.2	0.2	ALPS
2/18/2009	ST2*	Dripwater	79.4	11.1	42.3	0.2	ALPS
3/17/2009	ST2*	Dripwater	75.4	10.8	41.9	0.2	DGS Q ICP-MS
3/17/2009	ST2*	Dripwater	76.5	10.5	42.2	0.2	DGS Q ICP-MS
4/14/2009	ST2	Dripwater	65.6	10.2	79.3	0.2	ALPS
5/13/2009	ST2*	Dripwater	75.8	10.4	42.3	0.2	ALPS
5/13/2009	ST2*	Dripwater	79.0	11.1	43.4	0.2	ALPS
5/13/2009	ST2*	Dripwater	78.4	10.8	42.6	0.2	ALPS
6/12/2009	ST2*	Dripwater	77.8	10.4	42.9	0.2	ALPS
6/12/2009	ST2*	Dripwater	79.1	11.0	43.3	0.2	ALPS
6/12/2009	ST2*	Dripwater	79.8	11.1	42.9	0.2	ALPS
7/15/2009	ST2*	Dripwater	74.5	10.4	42.5	0.1	DGS Q ICP-MS
7/15/2009	ST2*	Dripwater	75.4	10.8	43.4	0.2	DGS Q ICP-MS
8/22/2009	ST2*	Dripwater	76.8	10.4	43.8	0.1	ALPS

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Sample Date[a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
8/22/2009	ST2*	Dripwater	80.5	11.1	44.6	0.2	ALPS
8/22/2009	ST2*	Dripwater	77.3	10.8	42.3	0.2	ALPS
9/22/2009	ST2*	Dripwater	76.7	10.5	44.1	0.1	DGS Q ICP-MS
9/22/2009	ST2*	Dripwater	77.8	10.8	43.4	0.2	DGS Q ICP-MS
10/21/2009	ST2*	Dripwater	76.3	10.3	43.2	0.1	ALPS
10/21/2009	ST2*	Dripwater	78.0	10.8	42.4	0.2	ALPS
10/21/2009	ST2*	Dripwater	79.8	11.0	43.3	0.2	ALPS
11/24/2009	ST2	Dripwater	78.1	10.9	43.4	0.2	DGS Q ICP-MS
12/22/2009	ST2	Dripwater	76.6	10.7	41.5	0.2	DGS Q ICP-MS
1/26/2010	ST2	Dripwater	74.2	10.9	42.0	0.2	DGS Q ICP-MS
3/2/2010	ST2	Dripwater	75.9	10.7	40.7	0.2	DGS Q ICP-MS
4/6/2010	ST2	Dripwater	77.6	10.6	40.0	0.2	DGS Q ICP-MS
5/4/2010	ST2	Dripwater	77.9	10.6	39.3	0.2	DGS Q ICP-MS
6/8/2010	ST2	Dripwater	76.0	10.5	38.9	0.2	DGS Q ICP-MS
7/13/2010	ST2	Dripwater	75.3	10.5	39.5	0.2	DGS Q ICP-MS
8/17/2010	ST2	Dripwater	79.5	10.6	40.2	0.2	DGS Q ICP-MS
9/28/2010	ST2	Dripwater	77.5	10.7	40.0	0.2	DGS Q ICP-MS
10/26/2010	ST2	Dripwater	78.3	10.7	39.8	0.2	DGS Q ICP-MS
11/23/2010	ST2	Dripwater	78.6	10.6	39.9	0.2	ALPS
12/21/2010	ST2	Dripwater	78.2	10.8	39.9	0.2	ALPS
1/25/2011	ST2	Dripwater	77.4	11.0	40.6	0.2	ALPS
2/22/2011	ST2	Dripwater	82.6	10.6	38.7	0.2	ALPS
3/29/2011	ST2	Dripwater	77.0	10.6	38.6	0.2	ALPS
4/26/2011	ST2	Dripwater	46.1	10.8	36.8	0.2	ALPS
5/24/2011	ST2*	Dripwater	78.2	10.8	39.5	0.2	ALPS
5/24/2011	ST2*	Dripwater	81.3	11.1	40.7	0.2	ALPS
6/21/2011	ST2	Dripwater	79.8	11.0	39.8	0.2	ALPS
7/19/2011	ST2	Dripwater	81.4	11.1	40.6	0.2	ALPS
8/30/2011	ST2	Dripwater	64.9	11.0	40.6	0.2	ALPS
9/27/2011	ST2	Dripwater	80.5	11.1	38.9	0.2	ALPS
12/20/2011	ST2	Dripwater	77.3	11.0	38.3	0.2	ALPS
1/24/2012	ST2	Dripwater	85.2	12.4	35.6	0.2	ALPS
8/3/2012	ST2	Dripwater	75.0	10.1	34.7	0.1	DGS Q ICP-MS
8/28/2012	ST2	Dripwater	72.5	9.9	34.5	0.1	DGS Q ICP-MS
9/25/2012	ST2	Dripwater	75.9	10.1	35.2	0.1	DGS Q ICP-MS
10/23/2012	ST2	Dripwater	75.2	10.2	34.8	0.1	DGS Q ICP-MS
11/20/2012	ST2	Dripwater	75.4	10.2	35.0	0.1	DGS Q ICP-MS

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Sample Date[a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
12/22/2012	ST2	Dripwater	72.8	10.1	34.2	0.1	DGS Q ICP-MS
1/16/2013	ST2	Dripwater	69.8	10.1	33.7	0.1	DGS Q ICP-MS
3/19/2013	ST2*	Dripwater	26.0	9.2	25.9	0.1	DGS Q ICP-MS
3/19/2013	ST2*	Dripwater	72.6	10.0	33.2	0.1	DGS Q ICP-MS
4/23/2013	ST2	Dripwater	73.6	10.1	33.3	0.1	DGS Q ICP-MS
5/21/2013	ST2	Dripwater	75.2	10.1	33.3	0.1	DGS Q ICP-MS
6/26/2013	ST2	Dripwater	74.9	10.1	33.9	0.1	DGS Q ICP-MS
7/30/2013	ST2	Dripwater	74.0	10.0	33.8	0.1	DGS Q ICP-MS
8/27/2013	ST2	Dripwater	74.4	10.1	34.5	0.1	DGS Q ICP-MS
9/24/2013	ST2	Dripwater	73.3	10.0	34.2	0.1	DGS Q ICP-MS
10/22/2013	ST2	Dripwater	74.1	10.1	35.1	0.1	DGS Q ICP-MS
11/19/2013	ST2	Dripwater	73.8	10.1	35.2	0.1	DGS Q ICP-MS
12/17/2013	ST2*	Dripwater	43.6	9.2	22.6	0.1	DGS Q ICP-MS
12/17/2013	ST2*	Dripwater	31.9	9.6	34.0	0.1	DGS Q ICP-MS
1/21/2014	ST2	Dripwater	71.1	9.8	33.7	0.1	DGS Q ICP-MS
2/17/2014	ST2	Dripwater	74.7	10.0	33.8	0.1	DGS Q ICP-MS
4/23/2014	ST2	Dripwater	73.0	9.8	32.4	0.1	DGS Q ICP-MS
5/23/2014	ST2	Dripwater	73.3	9.8	32.3	0.1	DGS Q ICP-MS
6/18/2014	ST2	Dripwater	73.9	9.9	32.5	0.1	DGS Q ICP-MS
8/18/2014	ST2	Dripwater	74.2	9.4	30.9	0.1	DGS Q ICP-MS
9/23/2014	ST2	Dripwater	74.0	9.3	30.7	0.1	DGS Q ICP-MS
10/31/2014	ST2	Dripwater	74.0	9.3	30.4	0.1	DGS Q ICP-MS
9/23/2008	TRN*	Dripwater	49.6	9.3	31.8	0.2	DGS Q ICP-MS
9/23/2008	TRN*	Dripwater	50.8	9.4	31.9	0.2	DGS Q ICP-MS
10/21/2008	TRN*	Dripwater	53.6	9.1	31.2	0.2	ALPS
10/21/2008	TRN*	Dripwater	55.0	9.6	32.6	0.2	ALPS
11/18/2008	TRN*	Dripwater	53.0	9.6	31.0	0.2	DGS Q ICP-MS
11/18/2008	TRN*	Dripwater	53.5	9.8	31.0	0.2	DGS Q ICP-MS
12/16/2008	TRN*	Dripwater	49.6	9.4	29.9	0.2	ALPS
12/16/2008	TRN*	Dripwater	50.9	10.0	31.5	0.2	ALPS
1/13/2009	TRN*	Dripwater	45.5	9.5	30.9	0.2	DGS Q ICP-MS
1/13/2009	TRN*	Dripwater	46.9	9.7	31.6	0.2	DGS Q ICP-MS
2/18/2009	TRN*	Dripwater	40.5	9.5	65.7	0.2	DGS Q ICP-MS
2/18/2009	TRN*	Dripwater	41.9	9.2	31.3	0.2	DGS Q ICP-MS
3/17/2009	TRN*	Dripwater	38.3	9.2	64.2	0.2	ALPS
3/17/2009	TRN*	Dripwater	40.9	9.4	32.3	0.2	ALPS
4/14/2009	TRN*	Dripwater	39.1	9.3	64.2	0.2	DGS Q ICP-MS

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Sample Date [a, b]	**Site Name (Replicate*)**	**Site Type**	**Ca (ppm)**	**Mg (ppm)**	**Na (ppm)**	**Sr (ppm)**	**Lab**
4/14/2009	TRN*	Dripwater	42.3	9.4	32.6	0.2	DGS Q ICP-MS
5/13/2009	TRN*	Dripwater	48.2	9.5	33.2	0.2	ALPS
5/13/2009	TRN*	Dripwater	45.3	9.4	32.2	0.2	ALPS
5/13/2009	TRN*	Dripwater	45.6	9.4	31.6	0.2	ALPS
6/12/2009	TRN*	Dripwater	53.0	9.7	32.8	0.2	DGS Q ICP-MS
6/12/2009	TRN*	Dripwater	49.8	9.2	30.6	0.2	DGS Q ICP-MS
7/15/2009	TRN*	Dripwater	49.3	9.2	31.8	0.2	ALPS
7/15/2009	TRN*	Dripwater	50.0	9.3	31.5	0.2	ALPS
7/15/2009	TRN*	Dripwater	51.4	9.9	31.6	0.2	ALPS
8/22/2009	TRN*	Dripwater	51.2	9.3	32.2	0.2	ALPS
8/22/2009	TRN*	Dripwater	52.2	9.6	31.9	0.2	ALPS
8/22/2009	TRN*	Dripwater	53.8	10.0	32.1	0.2	ALPS
9/22/2009	TRN*	Dripwater	52.2	9.2	32.7	0.2	ALPS
9/22/2009	TRN*	Dripwater	52.6	9.6	32.1	0.2	ALPS
9/22/2009	TRN*	Dripwater	53.4	9.8	32.0	0.2	ALPS
10/21/2009	TRN*	Dripwater	53.2	9.5	33.7	0.2	DGS Q ICP-MS
10/21/2009	TRN*	Dripwater	53.4	9.8	32.1	0.2	DGS Q ICP-MS
11/24/2009	TRN	Dripwater	55.2	10.2	34.7	0.2	ALPS
12/22/2009	TRN	Dripwater	50.1	10.0	32.5	0.2	DGS Q ICP-MS
1/26/2010	TRN	Dripwater	46.5	9.9	34.5	0.2	ALPS
3/2/2010	TRN	Dripwater	43.3	9.4	33.0	0.2	ALPS
4/6/2010	TRN	Dripwater	42.5	9.2	33.6	0.2	DGS Q ICP-MS
5/4/2010	TRN	Dripwater	41.9	8.9	33.9	0.2	ALPS
6/8/2010	TRN	Dripwater	48.2	9.0	34.4	0.2	DGS Q ICP-MS
7/13/2010	TRN	Dripwater	48.3	9.0	33.2	0.2	DGS Q ICP-MS
8/17/2010	TRN	Dripwater	48.6	9.1	32.9	0.2	DGS Q ICP-MS
9/28/2010	TRN	Dripwater	49.7	9.5	33.5	0.2	DGS Q ICP-MS
10/26/2010	TRN	Dripwater	50.6	9.6	33.5	0.2	ALPS
11/23/2010	TRN	Dripwater	49.8	9.8	33.6	0.2	DGS Q ICP-MS
12/21/2010	TRN	Dripwater	47.9	9.6	33.2	0.2	ALPS
1/25/2011	TRN	Dripwater	43.5	9.6	33.6	0.2	ALPS
2/22/2011	TRN	Dripwater	39.2	8.9	31.6	0.2	ALPS
3/29/2011	TRN	Dripwater	39.9	9.4	33.8	0.2	ALPS
4/26/2011	TRN	Dripwater	43.3	9.2	32.9	0.2	DGS Q ICP-MS
5/24/2011	TRN	Dripwater	45.6	9.5	34.2	0.2	DGS Q ICP-MS
6/21/2011	TRN	Dripwater	50.3	9.8	34.1	0.2	ALPS
7/19/2011	TRN	Dripwater	54.5	9.9	32.7	0.2	ALPS

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Sample Date[a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
8/30/2011	TRN	Dripwater	51.1	10.4	33.6	0.2	ALPS
9/27/2011	TRN	Dripwater	58.8	10.6	33.3	0.2	ALPS
10/25/2011	TRN	Dripwater	60.4	11.0	33.8	0.2	ALPS
11/22/2011	TRN	Dripwater	60.1	10.7	33.4	0.2	ALPS
12/20/2011	TRN	Dripwater	53.3	10.6	34.7	0.2	ALPS
1/24/2012	TRN	Dripwater	49.8	10.4	34.4	0.2	ALPS
2/28/2012	TRN	Dripwater	43.3	9.2	32.8	0.2	ALPS
3/27/2012	TRN	Dripwater	40.9	8.9	32.8	0.2	ALPS
4/23/2012	TRN	Dripwater	41.4	8.8	32.9	0.2	ALPS
5/22/2012	TRN	Dripwater	43.7	8.8	32.5	0.2	ALPS
6/29/2012	TRN	Dripwater	49.8	9.1	33.1	0.2	ALPS
7/31/2012	TRN	Dripwater	49.2	9.1	32.3	0.2	ALPS
8/28/2012	TRN	Dripwater	48.4	9.1	32.4	0.2	ALPS
9/25/2012	TRN	Dripwater	50.6	9.1	31.7	0.2	ALPS
10/23/2012	TRN	Dripwater	53.7	9.0	34.2	0.2	ALPS
11/20/2012	TRN	Dripwater	52.5	9.6	34.4	0.2	ALPS
12/22/2012	TRN	Dripwater	46.7	9.4	32.9	0.2	ALPS
1/16/2013	TRN	Dripwater	44.4	9.2	32.9	0.2	ALPS
3/19/2013	TRN	Dripwater	38.8	8.6	32.0	0.2	ALPS
4/23/2013	TRN	Dripwater	40.2	8.7	32.3	0.2	ALPS
5/21/2013	TRN	Dripwater	46.1	8.9	32.5	0.2	ALPS
6/26/2013	TRN	Dripwater	46.5	8.9	31.8	0.2	ALPS
7/30/2013	TRN	Dripwater	48.9	9.1	31.9	0.2	ALPS
8/27/2013	TRN	Dripwater	48.0	9.1	31.7	0.2	ALPS
9/24/2013	TRN	Dripwater	47.4	9.1	31.6	0.2	ALPS
10/22/2013	TRN	Dripwater	51.4	8.0	28.4	0.2	ALPS
11/19/2013	TRN	Dripwater	48.6	9.2	32.3	0.2	ALPS
12/17/2013	TRN	Dripwater	9.0	1.7	6.0	0.0	ALPS
1/21/2014	TRN	Dripwater	42.8	8.9	30.6	0.2	ALPS
2/17/2014	TRN	Dripwater	7.2	1.6	5.8	0.0	ALPS
3/18/2014	TRN	Dripwater	40.7	8.7	30.6	0.2	ALPS
4/23/2014	TRN	Dripwater	41.1	8.4	30.0	0.2	ALPS
5/23/2014	TRN	Dripwater	44.5	8.6	30.4	0.2	ALPS
6/17/2014	TRN	Dripwater	48.3	8.5	29.7	0.2	ALPS
8/18/2014	TRN	Dripwater	49.3	8.9	27.8	0.2	ALPS
10/31/2014	TRN	Dripwater	54.0	9.0	27.6	0.2	ALPS
11/29/2014	TRN	Dripwater	50.1	9.1	29.1	0.2	ALPS

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Sample Date[a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
12/30/2014	TRN	Dripwater	47.3	8.9	26.3	0.2	ALPS
1/31/2015	TRN	Dripwater	44.5	8.7	26.3	0.2	ALPS
2/28/2015	TRN	Dripwater	40.0	8.4	25.5	0.2	ALPS
3/28/2015	TRN	Dripwater	37.8	8.2	25.8	0.2	DGS Q ICP-MS
5/2/2015	TRN	Dripwater	37.1	8.0	25.9	0.1	DGS Q ICP-MS
5/30/2015	TRN	Dripwater	37.3	7.9	26.0	0.1	DGS Q ICP-MS
6/26/2015	TRN	Dripwater	38.4	8.1	26.6	0.1	DGS Q ICP-MS
7/30/2015	TRN	Dripwater	45.7	8.5	24.2	0.2	DGS Q ICP-MS
9/1/2015	TRN*	Dripwater	36.4	9.3	23.8	0.1	DGS Q ICP-MS
9/1/2015	TRN*	Dripwater	52.6	8.3	23.8	0.2	DGS Q ICP-MS
9/29/2015	TRN	Dripwater	53.2	8.4	22.5	0.2	DGS Q ICP-MS
10/27/2015	TRN	Dripwater	56.1	8.6	23.0	0.2	DGS Q ICP-MS
11/24/2015	TRN	Dripwater	51.6	8.8	22.8	0.2	DGS Q ICP-MS
12/29/2015	TRN	Dripwater	45.1	8.4	22.3	0.2	DGS Q ICP-MS
11/6/2013	A10	Well	92.1	19.7	161.0	0.7	DGS Q ICP-MS
1/31/2014	A10	Well	135.8	22.9	179.4	0.8	DGS Q ICP-MS
5/8/2014	A10	Well	138.8	21.2	186.4	0.8	DGS Q ICP-MS
8/14/2014	A10	Well	140.0	21.3	184.8	0.8	DGS Q ICP-MS
10/23/2014	A10	Well	138.2	18.6	158.9	0.7	DGS Q ICP-MS
1/29/2015	A10	Well	142.8	20.9	170.0	0.8	DGS Q ICP-MS
11/6/2013	AG2A	Well	49.3	2.8	15.4	0.1	DGS Q ICP-MS
5/8/2014	AG2A	Well	67.9	2.7	13.2	0.1	DGS Q ICP-MS
8/14/2014	AG2A	Well	71.2	2.8	12.7	0.1	DGS Q ICP-MS
10/23/2014	AG2A	Well	72.6	2.8	12.7	0.1	DGS Q ICP-MS
1/29/2015	AG2A	Well	75.6	2.7	12.0	0.1	DGS Q ICP-MS
11/6/2013	D14	Well	56.5	4.4	35.9	0.1	DGS Q ICP-MS
1/31/2014	D14	Well	91.7	4.9	39.1	0.1	DGS Q ICP-MS
5/8/2014	D14	Well	78.9	4.5	37.2	0.1	DGS Q ICP-MS
8/14/2014	D14	Well	81.5	4.9	38.6	0.1	DGS Q ICP-MS
10/23/2014	D14	Well	84.0	4.7	39.9	0.1	DGS Q ICP-MS
1/29/2015	D14	Well	83.6	4.6	35.9	0.1	DGS Q ICP-MS
11/6/2013	F02	Well	52.9	9.2	76.7	0.1	DGS Q ICP-MS
1/31/2014	F02	Well	79.7	9.6	78.0	0.1	DGS Q ICP-MS
5/8/2014	F02	Well	76.9	9.9	76.3	0.1	DGS Q ICP-MS
8/14/2014	F02	Well	77.7	9.2	76.5	0.1	DGS Q ICP-MS
10/23/2014	F02	Well	78.6	9.0	76.9	0.1	DGS Q ICP-MS
1/29/2015	F02	Well	79.9	10.1	81.1	0.2	DGS Q ICP-MS

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Sample Date[a, b]	Site Name (Replicate*)	Site Type	Ca (ppm)	Mg (ppm)	Na (ppm)	Sr (ppm)	Lab
11/6/2013	M04	Well	46.1	9.1	16.6	0.1	DGS Q ICP-MS
1/31/2014	M04	Well	64.1	11.2	16.2	0.2	DGS Q ICP-MS
5/8/2014	M04	Well	67.7	10.6	16.3	0.2	DGS Q ICP-MS
8/14/2014	M04	Well	67.9	7.9	14.5	0.1	DGS Q ICP-MS
10/23/2014	M04	Well	65.8	9.1	15.5	0.1	DGS Q ICP-MS
1/29/2015	M04	Well	61.4	12.1	14.5	0.2	DGS Q ICP-MS
11/6/2013	M18	Well	46.7	4.1	26.7	0.2	DGS Q ICP-MS
1/31/2014	M18	Well	74.9	4.3	26.2	0.3	DGS Q ICP-MS
5/8/2014	M18	Well	81.2	5.8	36.7	0.3	DGS Q ICP-MS
8/14/2014	M18	Well	76.1	4.7	27.0	0.3	DGS Q ICP-MS
10/23/2014	M18	Well	77.5	4.2	26.4	0.3	DGS Q ICP-MS
1/29/2015	M18	Well	80.5	4.6	26.1	0.3	DGS Q ICP-MS
11/6/2013	Y02	Well	58.9	6.4	17.5	0.1	DGS Q ICP-MS
1/31/2014	Y02	Well	84.5	6.2	16.8	0.1	DGS Q ICP-MS
5/8/2014	Y02	Well	84.9	6.4	16.4	0.1	DGS Q ICP-MS
8/14/2014	Y02	Well	86.0	6.2	15.8	0.1	DGS Q ICP-MS
10/23/2014	Y02	Well	89.3	6.1	16.7	0.1	DGS Q ICP-MS
1/29/2015	Y02	Well	89.7	6.6	15.3	0.1	DGS Q ICP-MS
11/6/2013	Y07	Well	64.6	7.0	13.0	0.1	DGS Q ICP-MS
1/31/2014	Y07	Well	96.2	7.6	13.4	0.1	DGS Q ICP-MS
5/8/2014	Y07	Well	93.3	7.8	12.8	0.1	DGS Q ICP-MS
8/14/2014	Y07	Well	96.3	7.5	13.0	0.1	DGS Q ICP-MS
10/23/2014	Y07	Well	99.4	7.6	13.8	0.1	DGS Q ICP-MS
1/29/2015	Y07	Well	101.3	7.0	13.0	0.1	DGS Q ICP-MS
11/6/2013	Y15	Well	39.9	2.4	9.1	0.1	DGS Q ICP-MS
1/31/2014	Y15	Well	59.1	2.7	9.6	0.1	DGS Q ICP-MS
5/8/2014	Y15	Well	60.8	2.7	10.3	0.1	DGS Q ICP-MS
8/14/2014	Y15	Well	57.5	2.5	8.6	0.1	DGS Q ICP-MS
10/23/2014	Y15	Well	58.9	2.4	8.4	0.1	DGS Q ICP-MS
1/29/2015	Y15	Well	63.6	2.7	9.4	0.1	DGS Q ICP-MS
11/6/2013	Y23	Well	62.0	3.8	11.6	0.1	DGS Q ICP-MS
1/31/2014	Y23	Well	93.9	3.8	11.4	0.1	DGS Q ICP-MS
5/8/2014	Y23	Well	88.8	3.7	11.0	0.1	DGS Q ICP-MS
8/14/2014	Y23	Well	92.1	3.8	11.0	0.1	DGS Q ICP-MS
10/23/2014	Y23	Well	90.3	3.6	10.9	0.1	DGS Q ICP-MS
1/29/2015	Y23	Well	92.9	3.7	10.4	0.1	DGS Q ICP-MS

[a, b] Cave dripwater cation data from 07/2008 to 11/2010 obtained from Partin et al. (2012) and Noronha et al. (2016), and data from 11/2010 to 01/2016 obtained from Noronha et al. (2016).

ALPS - Analytic Lab for Paleoclimate Studies; DGS Q ICP-MS - Department of Geosciences Quadrupole Inductively Coupled Plasma-Mass Spectrometry

Table S1.3 Cave dripwater, rainwater, and groundwater stable isotope compositions

Sample Date [a]	**Site Name (Replicate*)**	**Site Type**	**$\delta^{18}O$ (‰ VSMOW)**	**δD (‰ VSMOW)**	**Lab ($\delta^{18}O$)**	**Lab (δD)**
9/23/2008	FTM	Dripwater	-6.1	-37	ALPS	ALPS
10/21/2008	FTM	Dripwater	-4.9	-31	ALPS	ALPS
11/18/2008	FTM	Dripwater	-6.2	-33	ALPS	ALPS
12/16/2008	FTM	Dripwater	-6.4	-32	ALPS	ALPS
1/13/2009	FTM*	Dripwater	-6.2	-36	SIL CZG	ALPS
1/13/2009	FTM*	Dripwater	-6.2		SIL CZG	
2/18/2009	FTM	Dripwater	-6.3	-34	ALPS	ALPS
3/17/2009	FTM*	Dripwater	-6.2	-33	SIL CZG	ALPS
3/17/2009	FTM*	Dripwater	-5.4		SIL CZG	
3/17/2009	FTM*	Dripwater	-6.1		SIL CZG	
4/14/2009	FTM	Dripwater	-6.1	-33	ALPS	ALPS
6/12/2009	FTM*	Dripwater	-6.2	-39	SIL CZG	ALPS
6/12/2009	FTM*	Dripwater	-6.2		SIL CZG	
8/22/2009	FTM*	Dripwater	-5.4	-36	SIL CZG	ALPS
8/22/2009	FTM*	Dripwater	-6.2		SIL CZG	
8/22/2009	FTM*	Dripwater	-6.1		SIL CZG	
8/22/2009	FTM*	Dripwater	-5.9		SIL CZG	
10/21/2009	FTM	Dripwater	-5.5	-30	ALPS	ALPS
11/24/2009	FTM	Dripwater	-5.5	-37	ALPS	ALPS
12/22/2009	FTM	Dripwater	-5.7	-32	ALPS	ALPS
1/26/2010	FTM	Dripwater	-5.8	-33	ALPS	ALPS
3/2/2010	FTM	Dripwater	-5.7		SIL CZG	
4/6/2010	FTM*	Dripwater	-5.7	-42	SIL CZG	ALPS
4/6/2010	FTM*	Dripwater	-5.8		SIL CZG	
5/4/2010	FTM	Dripwater	-5.7	-32	ALPS	ALPS
6/8/2010	FTM	Dripwater	-5.7	-39	ALPS	ALPS
7/13/2010	FTM	Dripwater	-5.8	-36	ALPS	ALPS
8/17/2010	FTM	Dripwater	-5.8	-38	ALPS	ALPS
9/28/2010	FTM*	Dripwater	-5.6	-42	SIL CZG	ALPS
9/28/2010	FTM*	Dripwater	-5.8		SIL CZG	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
10/26/2010	FTM	Dripwater	-5.9	-37	ALPS	ALPS
11/23/2010	FTM	Dripwater	-5.9	-36	ALPS	ALPS
12/21/2010	FTM	Dripwater	-5.9	-38	ALPS	ALPS
1/25/2011	FTM	Dripwater	-5.8		SIL CZG	
6/21/2011	FTM	Dripwater	-5.6		SIL CZG	
10/25/2011	FTM	Dripwater	-5.2		SIL CZG	
12/20/2011	FTM*	Dripwater	-6.1		SIL CZG	
12/20/2011	FTM*	Dripwater	-6.1		SIL CZG	
1/24/2012	FTM*	Dripwater	-5.7		SIL CZG	
1/24/2012	FTM*	Dripwater	-5.7		SIL CZG	
4/23/2012	FTM	Dripwater	-5.4		SIL CZG	
5/22/2012	FTM	Dripwater	-5.7		SIL CZG	
6/29/2012	FTM	Dripwater	-5.6		SIL CZG	
7/31/2012	FTM	Dripwater	-5.4		SIL CZG	
8/28/2012	FTM*	Dripwater	-5.7		SIL CZG	
8/28/2012	FTM*	Dripwater	-5.7		SIL CZG	
9/25/2012	FTM	Dripwater	-6.3		SIL CZG	
10/23/2012	FTM	Dripwater	-6.1		SIL CZG	
11/20/2012	FTM	Dripwater	-6.2		SIL CZG	
12/22/2012	FTM	Dripwater	-6.1		SIL CZG	
1/16/2013	FTM	Dripwater	-6.0		SIL CZG	
2/19/2013	FTM	Dripwater	-6.1		SIL CZG	
3/19/2013	FTM	Dripwater	-5.4		SIL CZG	
4/23/2013	FTM	Dripwater	-6.0		SIL CZG	
5/21/2013	FTM	Dripwater	-5.6		SIL CZG	
6/26/2013	FTM	Dripwater	-6.1		SIL CZG	
7/30/2013	FTM	Dripwater	-5.5		SIL CZG	
8/27/2013	FTM	Dripwater	-6.0		SIL CZG	
10/22/2013	FTM	Dripwater	-6.5		SIL CZG	
12/17/2013	FTM	Dripwater	-6.0		SIL CZG	
1/21/2014	FTM	Dripwater	-6.2		SIL CZG	
2/17/2014	FTM	Dripwater	-6.5		SIL CZG	
3/18/2014	FTM	Dripwater	-6.4		SIL CZG	
4/23/2014	FTM	Dripwater	-6.4		SIL CZG	
5/23/2014	FTM	Dripwater	-6.6		SIL CZG	
6/17/2014	FTM	Dripwater	-6.5		SIL CZG	
8/18/2014	FTM	Dripwater	-6.9		SIL CZG	
9/23/2014	FTM	Dripwater	-6.8		SIL CZG	
10/31/2014	FTM	Dripwater	-7.3		SIL CZG	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
11/29/2014	FTM	Dripwater	-7.1		SIL CZG	
12/30/2014	FTM	Dripwater	-7.1		SIL CZG	
1/31/2015	FTM	Dripwater	-7.2		SIL CZG	
2/28/2015	FTM	Dripwater	-7.3		SIL CZG	
3/28/2015	FTM	Dripwater	-5.2	-42	ALPS	ALPS
5/2/2015	FTM	Dripwater	-7.2	-46	ALPS	ALPS
5/30/2015	FTM	Dripwater	-6.6	-45	ALPS	ALPS
6/26/2015	FTM	Dripwater	-7.4	-47	ALPS	ALPS
7/30/2015	FTM	Dripwater	-7.2	-49	ALPS	ALPS
9/1/2015	FTM	Dripwater	-8.3	-55	ALPS	ALPS
9/29/2015	FTM	Dripwater	-8.5	-57	ALPS	ALPS
10/27/2015	FTM	Dripwater	-8.5	-57	ALPS	ALPS
11/24/2015	FTM	Dripwater	-8.1	-55	ALPS	ALPS
12/29/2015	FTM	Dripwater	-8.3	-55	ALPS	ALPS
9/23/2008	SMP*	Dripwater	-5.7	-46	SIL CZG	ALPS
9/23/2008	SMP*	Dripwater	-6.0		SIL CZG	
9/23/2008	SMP*	Dripwater	-6.5		SIL CZG	
10/21/2008	SMP*	Dripwater	-6.7	-43	SIL CZG	ALPS
10/21/2008	SMP*	Dripwater	-6.6		SIL CZG	
10/21/2008	SMP*	Dripwater	-6.5		SIL CZG	
10/21/2008	SMP*	Dripwater	-7.0		SIL CZG	
11/18/2008	SMP*	Dripwater	-6.4	-44	ALPS	ALPS
11/18/2008	SMP*	Dripwater	-6.5		ALPS	
12/16/2008	SMP*	Dripwater	-6.1	-40	ALPS	ALPS
12/16/2008	SMP*	Dripwater	-6.4		ALPS	
1/13/2009	SMP*	Dripwater	-5.9	-36	ALPS	ALPS
1/13/2009	SMP*	Dripwater	-6.3		ALPS	
2/18/2009	SMP*	Dripwater	-5.6	-33	SIL CZG	ALPS
2/18/2009	SMP*	Dripwater	-5.5		SIL CZG	
2/18/2009	SMP*	Dripwater	-5.5		SIL CZG	
3/17/2009	SMP*	Dripwater	-5.8	-35	ALPS	ALPS
3/17/2009	SMP*	Dripwater	-5.6		ALPS	
4/14/2009	SMP*	Dripwater	-5.7	-36	ALPS	ALPS
4/14/2009	SMP*	Dripwater	-5.6		ALPS	
5/13/2009	SMP	Dripwater	-6.1	-38	ALPS	ALPS
6/12/2009	SMP	Dripwater	-6.2	-39	ALPS	ALPS
7/15/2009	SMP*	Dripwater	-6.6	-40	SIL CZG	ALPS
7/15/2009	SMP*	Dripwater	-6.7		SIL CZG	
7/15/2009	SMP*	Dripwater	-6.4		SIL CZG	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
7/15/2009	SMP*	Dripwater	-6.3		SIL CZG	
8/22/2009	SMP	Dripwater	-6.4	-40	ALPS	ALPS
9/22/2009	SMP	Dripwater	-6.4	-44	ALPS	ALPS
10/21/2009	SMP	Dripwater	-6.4	-42	ALPS	ALPS
11/24/2009	SMP*	Dripwater	-6.7	-41	SIL CZG	ALPS
11/24/2009	SMP*	Dripwater	-6.4		SIL CZG	
11/24/2009	SMP*	Dripwater	-6.7		SIL CZG	
11/24/2009	SMP*	Dripwater	-6.0		SIL CZG	
12/22/2009	SMP*	Dripwater	-6.1	-39	SIL CZG	ALPS
12/22/2009	SMP*	Dripwater	-6.4		SIL CZG	
1/26/2010	SMP*	Dripwater	-5.9	-37	SIL CZG	ALPS
1/26/2010	SMP*	Dripwater	-6.0		SIL CZG	
1/26/2010	SMP*	Dripwater	-5.9		SIL CZG	
4/6/2010	SMP*	Dripwater	-5.7	-36	SIL CZG	ALPS
4/6/2010	SMP*	Dripwater	-5.8		SIL CZG	
5/4/2010	SMP	Dripwater	-5.7	-37	ALPS	ALPS
6/8/2010	SMP*	Dripwater	-6.1	-42	SIL CZG	ALPS
6/8/2010	SMP*	Dripwater	-6.2		SIL CZG	
7/13/2010	SMP	Dripwater	-6.0	-37	ALPS	ALPS
8/17/2010	SMP*	Dripwater	-6.3	-42	SIL CZG	ALPS
8/17/2010	SMP*	Dripwater	-6.4		SIL CZG	
8/17/2010	SMP*	Dripwater	-6.3		SIL CZG	
8/17/2010	SMP*	Dripwater	-6.3		SIL CZG	
9/28/2010	SMP	Dripwater	-6.2	-38	ALPS	ALPS
10/26/2010	SMP	Dripwater	-6.1	-40	ALPS	ALPS
12/21/2010	SMP*	Dripwater	-5.6		SIL CZG	
12/21/2010	SMP*	Dripwater	-5.7		SIL CZG	
2/22/2011	SMP	Dripwater	-5.7		SIL CZG	
10/25/2011	SMP	Dripwater	-6.4		SIL CZG	
11/22/2011	SMP	Dripwater	-6.6		SIL CZG	
12/20/2011	SMP	Dripwater	-5.6		SIL CZG	
2/28/2012	SMP	Dripwater	-5.9		SIL CZG	
4/23/2012	SMP	Dripwater	-6.2		SIL CZG	
5/22/2012	SMP*	Dripwater	-6.0		SIL CZG	
5/22/2012	SMP*	Dripwater	-6.2		SIL CZG	
7/31/2012	SMP	Dripwater	-6.3		SIL CZG	
8/28/2012	SMP	Dripwater	-6.3		SIL CZG	
9/25/2012	SMP*	Dripwater	-6.0		SIL CZG	
9/25/2012	SMP*	Dripwater	-6.0		SIL CZG	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
11/20/2012	SMP*	Dripwater	-7.0		SIL CZG	
11/20/2012	SMP*	Dripwater	-6.5		SIL CZG	
11/20/2012	SMP*	Dripwater	-6.6		SIL CZG	
12/22/2012	SMP*	Dripwater	-6.4		SIL CZG	
12/22/2012	SMP*	Dripwater	-6.3		SIL CZG	
1/16/2013	SMP	Dripwater	-3.2		SIL CZG	
2/19/2013	SMP	Dripwater	-6.2		SIL CZG	
3/19/2013	SMP	Dripwater	-6.4		SIL CZG	
4/23/2013	SMP	Dripwater	-6.2		SIL CZG	
5/21/2013	SMP	Dripwater	-6.4		SIL CZG	
6/26/2013	SMP	Dripwater	-6.5		SIL CZG	
7/30/2013	SMP	Dripwater	-6.1		SIL CZG	
8/27/2013	SMP	Dripwater	-6.0		SIL CZG	
9/24/2013	SMP*	Dripwater	-5.4		SIL CZG	
9/24/2013	SMP*	Dripwater	-6.5		SIL CZG	
9/24/2013	SMP*	Dripwater	-6.2		SIL CZG	
10/22/2013	SMP	Dripwater	-6.0		SIL CZG	
11/19/2013	SMP	Dripwater	-6.3		SIL CZG	
12/17/2013	SMP	Dripwater	-6.1		SIL CZG	
1/21/2014	SMP	Dripwater	-6.3		SIL CZG	
2/17/2014	SMP	Dripwater	-6.7		SIL CZG	
3/18/2014	SMP	Dripwater	-6.6		SIL CZG	
4/23/2014	SMP	Dripwater	-6.5		SIL CZG	
5/23/2014	SMP*	Dripwater	-6.7		SIL CZG	
5/23/2014	SMP*	Dripwater	-6.6		SIL CZG	
6/17/2014	SMP	Dripwater	-6.5		SIL CZG	
8/18/2014	SMP	Dripwater	-6.4		SIL CZG	
9/23/2014	SMP*	Dripwater	-6.8		SIL CZG	
9/23/2014	SMP*	Dripwater	-6.7		SIL CZG	
10/31/2014	SMP	Dripwater	-6.7		SIL CZG	
11/29/2014	SMP	Dripwater	-6.6		SIL CZG	
12/30/2014	SMP	Dripwater	-6.4		SIL CZG	
1/31/2015	SMP	Dripwater	-6.5		SIL CZG	
2/28/2015	SMP	Dripwater	-6.4		SIL CZG	
3/28/2015	SMP	Dripwater	-4.5	-39	ALPS	ALPS
5/30/2015	SMP	Dripwater	-5.9	-41	ALPS	ALPS
6/26/2015	SMP	Dripwater	-5.5	-41	ALPS	ALPS
7/30/2015	SMP	Dripwater	-6.7	-44	ALPS	ALPS
9/1/2015	SMP	Dripwater	-7.1	-45	ALPS	ALPS

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
10/27/2015	SMP	Dripwater	-7.3	-46	ALPS	ALPS
11/24/2015	SMP	Dripwater	-7.1	-45	ALPS	ALPS
12/29/2015	SMP*	Dripwater	-7.2	-46	ALPS	ALPS
12/29/2015	SMP*	Dripwater	-7.0		ALPS	
1/17/2008	ST1	Dripwater	-6.0	-33	ALPS	ALPS
1/24/2008	ST1	Dripwater	-6.4	-34	ALPS	ALPS
2/8/2008	ST1	Dripwater	-6.3	-31	ALPS	ALPS
2/29/2008	ST1	Dripwater	-6.0	-32	ALPS	ALPS
3/7/2008	ST1	Dripwater	-5.4	-27	ALPS	ALPS
3/14/2008	ST1	Dripwater	-5.8	-31	ALPS	ALPS
5/27/2008	ST1	Dripwater	-6.5	-35	ALPS	ALPS
7/21/2008	ST1	Dripwater	-6.8	-36	ALPS	ALPS
8/15/2008	ST1*	Dripwater	-6.6	-43	ALPS	ALPS
8/15/2008	ST1*	Dripwater	-6.5		ALPS	
9/23/2008	ST1	Dripwater	-5.9	-40	ALPS	ALPS
10/21/2008	ST1*	Dripwater	-6.1	-42	ALPS	ALPS
10/21/2008	ST1*	Dripwater	-6.2		ALPS	
11/18/2008	ST1*	Dripwater	-6.3	-39	SIL CZG	ALPS
11/18/2008	ST1*	Dripwater	-6.3		SIL CZG	
11/18/2008	ST1*	Dripwater	-6.2		SIL CZG	
11/18/2008	ST1*	Dripwater	-6.5		SIL CZG	
12/16/2008	ST1*	Dripwater	-5.9	-37	ALPS	ALPS
12/16/2008	ST1*	Dripwater	-6.1		ALPS	
1/13/2009	ST1*	Dripwater	-5.2	-37	ALPS	ALPS
1/13/2009	ST1*	Dripwater	-5.4		ALPS	
2/18/2009	ST1*	Dripwater	-5.0	-32	ALPS	ALPS
2/18/2009	ST1*	Dripwater	-4.9		ALPS	
3/17/2009	ST1*	Dripwater	-5.8	-34	SIL CZG	ALPS
3/17/2009	ST1*	Dripwater	-5.6		SIL CZG	
3/17/2009	ST1*	Dripwater	-5.3		SIL CZG	
4/14/2009	ST1*	Dripwater	-5.3	-33	ALPS	ALPS
4/14/2009	ST1*	Dripwater	-5.2		ALPS	
5/13/2009	ST1	Dripwater	-6.1	-40	ALPS	ALPS
6/12/2009	ST1	Dripwater	-6.1	-37	ALPS	ALPS
7/15/2009	ST1	Dripwater	-6.2	-39	ALPS	ALPS
8/22/2009	ST1	Dripwater	-6.3	-41	ALPS	ALPS
9/22/2009	ST1	Dripwater	-6.5	-40	ALPS	ALPS
10/21/2009	ST1	Dripwater	-6.4	-44	ALPS	ALPS
11/24/2009	ST1	Dripwater	-6.0	-39	ALPS	ALPS

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
12/22/2009	ST1*	Dripwater	-6.1	-43	SIL CZG	ALPS
12/22/2009	ST1*	Dripwater	-6.0		SIL CZG	
1/26/2010	ST1	Dripwater	-5.8	-35	ALPS	ALPS
4/6/2010	ST1	Dripwater	-4.9	-28	ALPS	ALPS
5/4/2010	ST1*	Dripwater	-5.6	-37	SIL CZG	ALPS
5/4/2010	ST1*	Dripwater	-5.7		SIL CZG	
5/4/2010	ST1*	Dripwater	-5.5		SIL CZG	
6/8/2010	ST1*	Dripwater	-5.0	-40	SIL CZG	ALPS
6/8/2010	ST1*	Dripwater	-6.1		SIL CZG	
7/13/2010	ST1	Dripwater	-6.2	-40	ALPS	ALPS
8/17/2010	ST1	Dripwater	-6.1	-38	SIL CZG	ALPS
9/28/2010	ST1	Dripwater	-5.7	-36	ALPS	ALPS
10/26/2010	ST1	Dripwater	-5.9	-36	ALPS	ALPS
11/23/2010	ST1*	Dripwater	-5.8	-37	SIL CZG	ALPS
11/23/2010	ST1*	Dripwater	-6.4		SIL CZG	
11/23/2010	ST1*	Dripwater	-5.9		SIL CZG	
12/21/2010	ST1	Dripwater	-5.9		SIL CZG	
1/25/2011	ST1	Dripwater	-4.8		SIL CZG	
2/22/2011	ST1	Dripwater	-5.3		SIL CZG	
3/29/2011	ST1	Dripwater	-5.9		SIL CZG	
4/26/2011	ST1	Dripwater	-6.4		SIL CZG	
5/24/2011	ST1	Dripwater	-6.1		SIL CZG	
6/21/2011	ST1	Dripwater	-5.7		SIL CZG	
7/19/2011	ST1	Dripwater	-6.2		SIL CZG	
8/30/2011	ST1	Dripwater	-5.7		SIL CZG	
9/27/2011	ST1	Dripwater	-6.3		SIL CZG	
10/25/2011	ST1	Dripwater	-6.1		SIL CZG	
11/22/2011	ST1	Dripwater	-6.6		SIL CZG	
12/20/2011	ST1	Dripwater	-5.8		SIL CZG	
1/24/2012	ST1*	Dripwater	-5.4		SIL CZG	
1/24/2012	ST1*	Dripwater	-6.0		SIL CZG	
2/28/2012	ST1	Dripwater	-5.8		SIL CZG	
3/27/2012	ST1	Dripwater	-5.2		SIL CZG	
5/22/2012	ST1	Dripwater	-6.2		SIL CZG	
7/31/2012	ST1	Dripwater	-6.2		SIL CZG	
8/28/2012	ST1	Dripwater	-6.4		SIL CZG	
9/25/2012	ST1	Dripwater	-6.4		SIL CZG	
10/23/2012	ST1	Dripwater	-6.7		SIL CZG	
11/20/2012	ST1	Dripwater	-5.1		SIL CZG	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
12/22/2012	ST1	Dripwater	-5.5		SIL CZG	
1/16/2013	ST1	Dripwater	-4.6		SIL CZG	
2/19/2013	ST1	Dripwater	-4.7		SIL CZG	
3/19/2013	ST1	Dripwater	-4.9		SIL CZG	
4/23/2013	ST1	Dripwater	-4.6		SIL CZG	
5/21/2013	ST1	Dripwater	-6.0		SIL CZG	
6/26/2013	ST1	Dripwater	-6.1		SIL CZG	
7/30/2013	ST1	Dripwater	-6.2		SIL CZG	
8/27/2013	ST1	Dripwater	-6.2		SIL CZG	
9/24/2013	ST1	Dripwater	-6.2		SIL CZG	
10/22/2013	ST1	Dripwater	-5.9		SIL CZG	
11/19/2013	ST1	Dripwater	-6.6		SIL CZG	
12/17/2013	ST1	Dripwater	-6.3		SIL CZG	
2/17/2014	ST1	Dripwater	-5.3		SIL CZG	
3/18/2014	ST1	Dripwater	-6.3		SIL CZG	
4/23/2014	ST1	Dripwater	-6.1		SIL CZG	
5/23/2014	ST1	Dripwater	-6.6		SIL CZG	
6/17/2014	ST1	Dripwater	-6.5		SIL CZG	
8/18/2014	ST1*	Dripwater	-6.9		SIL CZG	
8/18/2014	ST1*	Dripwater	-6.9		SIL CZG	
9/23/2014	ST1*	Dripwater	-7.7		SIL CZG	
9/23/2014	ST1*	Dripwater	-7.6		SIL CZG	
10/31/2014	ST1	Dripwater	-7.5		SIL CZG	
11/29/2014	ST1	Dripwater	-7.2		SIL CZG	
12/30/2014	ST1	Dripwater	-6.3		SIL CZG	
1/31/2015	ST1	Dripwater	-7.0		SIL CZG	
2/28/2015	ST1	Dripwater	-6.8		SIL CZG	
3/28/2015	ST1	Dripwater	-5.5	-39	ALPS	ALPS
5/2/2015	ST1	Dripwater	-6.1	-39	ALPS	ALPS
5/30/2015	ST1	Dripwater	-7.0	-46	ALPS	ALPS
6/26/2015	ST1	Dripwater	-7.0	-45	ALPS	ALPS
7/30/2015	ST1	Dripwater	-8.2	-54	ALPS	ALPS
9/1/2015	ST1	Dripwater	-8.3	-55	ALPS	ALPS
9/29/2015	ST1	Dripwater	-8.4	-56	ALPS	ALPS
10/27/2015	ST1	Dripwater	-8.2	-55	ALPS	ALPS
11/24/2015	ST1	Dripwater	-7.1	-45	ALPS	ALPS
12/29/2015	ST1	Dripwater	-7.1	-46	ALPS	ALPS
9/23/2008	ST2*	Dripwater	-6.6	-44	ALPS	ALPS
9/23/2008	ST2*	Dripwater	-6.8		ALPS	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
10/21/2008	ST2*	Dripwater	-6.7	-43	ALPS	ALPS
10/21/2008	ST2*	Dripwater	-6.8		ALPS	
11/18/2008	ST2*	Dripwater	-6.6	-41	ALPS	ALPS
11/18/2008	ST2*	Dripwater	-6.6		ALPS	
12/16/2008	ST2*	Dripwater	-6.5	-46	ALPS	ALPS
12/16/2008	ST2*	Dripwater	-6.8		ALPS	
1/13/2009	ST2*	Dripwater	-6.5	-42	ALPS	ALPS
1/13/2009	ST2*	Dripwater	-6.7		ALPS	
2/18/2009	ST2*	Dripwater	-6.5	-46	ALPS	ALPS
2/18/2009	ST2*	Dripwater	-6.6		ALPS	
3/17/2009	ST2*	Dripwater	-6.5	-41	ALPS	ALPS
3/17/2009	ST2*	Dripwater	-6.5		ALPS	
4/14/2009	ST2*	Dripwater	-6.5	-45	ALPS	ALPS
4/14/2009	ST2*	Dripwater	-6.2		ALPS	
5/13/2009	ST2	Dripwater	-6.5	-42	ALPS	ALPS
6/12/2009	ST2	Dripwater	-6.4	-40	ALPS	ALPS
7/15/2009	ST2	Dripwater	-6.5	-40	ALPS	ALPS
8/22/2009	ST2	Dripwater	-6.5	-41	ALPS	ALPS
9/22/2009	ST2	Dripwater	-6.5	-41	ALPS	ALPS
10/21/2009	ST2	Dripwater	-6.5	-44	ALPS	ALPS
11/24/2009	ST2	Dripwater	-6.5	-42	ALPS	ALPS
12/22/2009	ST2	Dripwater	-6.5	-43	ALPS	ALPS
1/26/2010	ST2	Dripwater	-6.3	-41	ALPS	ALPS
4/6/2010	ST2	Dripwater	-6.4	-42	ALPS	ALPS
5/4/2010	ST2	Dripwater	-6.4	-41	ALPS	ALPS
6/8/2010	ST2	Dripwater	-6.5	-46	ALPS	ALPS
7/13/2010	ST2	Dripwater	-6.4	-43	ALPS	ALPS
8/17/2010	ST2	Dripwater	-6.5	-42	ALPS	ALPS
9/28/2010	ST2	Dripwater	-6.4	-43	ALPS	ALPS
10/26/2010	ST2	Dripwater	-6.5	-45	ALPS	ALPS
11/23/2010	ST2	Dripwater	-6.5	-41	ALPS	ALPS
12/21/2010	ST2	Dripwater	-6.4		SIL CZG	
1/25/2011	ST2	Dripwater	-6.4		SIL CZG	
2/22/2011	ST2	Dripwater	-6.3		SIL CZG	
3/29/2011	ST2	Dripwater	-6.4		SIL CZG	
4/26/2011	ST2	Dripwater	-5.9		SIL CZG	
5/24/2011	ST2	Dripwater	-6.2		SIL CZG	
6/21/2011	ST2	Dripwater	-6.2		SIL CZG	
8/30/2011	ST2	Dripwater	-6.6		SIL CZG	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
11/22/2011	ST2	Dripwater	-5.9		SIL CZG	
12/20/2011	ST2	Dripwater	-6.0		SIL CZG	
1/24/2012	ST2	Dripwater	-5.7		SIL CZG	
2/28/2012	ST2	Dripwater	-6.2		SIL CZG	
3/27/2012	ST2	Dripwater	-6.3		SIL CZG	
4/23/2012	ST2	Dripwater	-6.5		SIL CZG	
5/22/2012	ST2	Dripwater	-6.6		SIL CZG	
6/29/2012	ST2	Dripwater	-5.8		SIL CZG	
7/31/2012	ST2	Dripwater	-6.5		SIL CZG	
8/28/2012	ST2	Dripwater	-6.5		SIL CZG	
9/25/2012	ST2	Dripwater	-6.4		SIL CZG	
10/23/2012	ST2	Dripwater	-6.6		SIL CZG	
11/20/2012	ST2	Dripwater	-6.4		SIL CZG	
12/22/2012	ST2	Dripwater	-6.6		SIL CZG	
1/16/2013	ST2	Dripwater	-6.6		SIL CZG	
2/19/2013	ST2	Dripwater	-6.6		SIL CZG	
3/19/2013	ST2	Dripwater	-6.7		SIL CZG	
4/23/2013	ST2	Dripwater	-6.5		SIL CZG	
5/21/2013	ST2	Dripwater	-6.7		SIL CZG	
6/26/2013	ST2	Dripwater	-6.6		SIL CZG	
7/30/2013	ST2	Dripwater	-6.6		SIL CZG	
8/27/2013	ST2	Dripwater	-6.6		SIL CZG	
9/24/2013	ST2	Dripwater	-6.5		SIL CZG	
10/22/2013	ST2	Dripwater	-6.7		SIL CZG	
11/19/2013	ST2	Dripwater	-6.6		SIL CZG	
12/17/2013	ST2	Dripwater	-6.7		SIL CZG	
1/21/2014	ST2	Dripwater	-6.6		SIL CZG	
2/17/2014	ST2	Dripwater	-6.7		SIL CZG	
3/18/2014	ST2	Dripwater	-6.5		SIL CZG	
4/23/2014	ST2	Dripwater	-6.8		SIL CZG	
5/23/2014	ST2	Dripwater	-6.7		SIL CZG	
6/17/2014	ST2	Dripwater	-6.8		SIL CZG	
8/18/2014	ST2	Dripwater	-6.9		SIL CZG	
9/23/2014	ST2	Dripwater	-6.8		SIL CZG	
10/31/2014	ST2	Dripwater	-7.0		SIL CZG	
11/29/2014	ST2	Dripwater	-7.0		SIL CZG	
12/30/2014	ST2	Dripwater	-7.0		SIL CZG	
1/31/2015	ST2*	Dripwater	-6.8		SIL CZG	
1/31/2015	ST2*	Dripwater	-7.1		SIL CZG	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
2/28/2015	ST2	Dripwater	-7.0		SIL CZG	
3/28/2015	ST2	Dripwater	-7.0	-45	ALPS	ALPS
5/2/2015	ST2	Dripwater	-7.2	-46	ALPS	ALPS
5/30/2015	ST2	Dripwater	-7.4	-47	ALPS	ALPS
6/26/2015	ST2	Dripwater	-7.4	-47	ALPS	ALPS
9/1/2015	ST2	Dripwater	-7.4	-48	ALPS	ALPS
10/27/2015	ST2	Dripwater	-7.6	-49	ALPS	ALPS
11/24/2015	ST2	Dripwater	-7.6	-49	ALPS	ALPS
12/29/2015	ST2	Dripwater	-7.7	-50	ALPS	ALPS
12/31/1961	GNIP	Rain Water	-2.6	-7	UOC	UOC
1/31/1962	GNIP	Rain Water	-1.3	5	UOC	UOC
2/28/1962	GNIP	Rain Water	-3.8	-6	UOC	UOC
3/31/1962	GNIP	Rain Water	-1.4	2	UOC	UOC
4/30/1962	GNIP	Rain Water	-3.8	-29	UOC	UOC
5/31/1962	GNIP	Rain Water	-3.1	-16	UOC	UOC
6/30/1962	GNIP	Rain Water	-4.1	-11	UOC	UOC
7/31/1962	GNIP	Rain Water	-8.3	-56	UOC	UOC
8/31/1962	GNIP	Rain Water	-6.5	-30	UOC	UOC
9/30/1962	GNIP	Rain Water	-6.5	-32	UOC	UOC
10/31/1962	GNIP	Rain Water	-8.1	-43	UOC	UOC
11/30/1962	GNIP	Rain Water	-7.4	-46	UOC	UOC
12/31/1962	GNIP	Rain Water	-6.4	-39	UOC	UOC
1/31/1963	GNIP	Rain Water	-4.0	-12	UOC	UOC
2/28/1963	GNIP	Rain Water	-1.6	-7	UOC	UOC
3/31/1963	GNIP	Rain Water	-1.6	-10	UOC	UOC
4/30/1963	GNIP	Rain Water	-4.5	-32	UOC	UOC
5/31/1963	GNIP	Rain Water	-5.6	-39	UOC	UOC
6/30/1963	GNIP	Rain Water	-6.0	-40	UOC	UOC
7/31/1963	GNIP	Rain Water	-7.4	-49	UOC	UOC
8/31/1963	GNIP	Rain Water	-5.4	-32	UOC	UOC
9/30/1963	GNIP	Rain Water	-6.9	-46	UOC	UOC
10/31/1963	GNIP	Rain Water	-7.4	-53	UOC	UOC
11/30/1963	GNIP	Rain Water	-3.0	-13	UOC	UOC
12/31/1963	GNIP	Rain Water	-7.3	-47	UOC	UOC
1/31/1964	GNIP	Rain Water	-1.1	1	UOC	UOC
2/29/1964	GNIP	Rain Water	-0.8	3	UOC	UOC
3/31/1964	GNIP	Rain Water	-1.4	4	UOC	UOC
4/30/1964	GNIP	Rain Water	-4.5	-29	UOC	UOC
5/31/1964	GNIP	Rain Water	-6.7	-40	UOC	UOC

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
6/30/1964	GNIP	Rain Water	-3.9	-19	UOC	UOC
7/31/1964	GNIP	Rain Water	-4.5	-24	UOC	UOC
8/31/1964	GNIP	Rain Water	-7.2	-43	UOC	UOC
9/30/1964	GNIP	Rain Water	-8.8	-57	UOC	UOC
10/31/1964	GNIP	Rain Water	-6.9	-47	UOC	UOC
11/30/1964	GNIP	Rain Water	-4.4	-28	UOC	UOC
12/31/1964	GNIP	Rain Water	-2.8	-9	UOC	UOC
1/31/1965	GNIP	Rain Water	-4.5	-20	UOC	UOC
2/28/1965	GNIP	Rain Water	1.6	8	UOC	UOC
3/31/1965	GNIP	Rain Water	0.7	14	UOC	UOC
4/30/1965	GNIP	Rain Water	2.1	3	UOC	UOC
5/31/1965	GNIP	Rain Water	0.7	5	UOC	UOC
6/30/1965	GNIP	Rain Water	-2.1	-9	UOC	UOC
7/31/1965	GNIP	Rain Water	-5.2	-35	UOC	UOC
8/31/1965	GNIP	Rain Water	-1.9	-17	UOC	UOC
9/30/1965	GNIP	Rain Water	-9.4	-63	UOC	UOC
11/30/1965	GNIP	Rain Water	-1.1	-7	UOC	UOC
12/31/1965	GNIP	Rain Water	1.3	8	UOC	UOC
1/31/1966	GNIP	Rain Water	1.0	18	UOC	UOC
4/30/1966	GNIP	Rain Water	2.1	19	UOC	UOC
5/31/1966	GNIP	Rain Water	0.1	7	UOC	UOC
6/30/1966	GNIP	Rain Water	-2.2	-7	UOC	UOC
7/31/1966	GNIP	Rain Water	-3.4	-21	UOC	UOC
8/31/1966	GNIP	Rain Water	-8.9	-57	UOC	UOC
9/30/1966	GNIP	Rain Water	-6.9	-42	UOC	UOC
10/31/1966	GNIP	Rain Water	-3.9	-13	UOC	UOC
11/30/1966	GNIP	Rain Water	-0.6	4	UOC	UOC
12/31/1966	GNIP	Rain Water	-0.6	5	UOC	UOC
2/28/1973	GNIP	Rain Water	-0.5	6	IAEA	IAEA
3/31/1973	GNIP	Rain Water	-0.3	6	IAEA	IAEA
4/30/1973	GNIP	Rain Water	-0.2	4	IAEA	IAEA
5/31/1973	GNIP	Rain Water	-2.9	-14	IAEA	IAEA
6/30/1973	GNIP	Rain Water	-2.1	-10	IAEA	IAEA
7/31/1973	GNIP	Rain Water	-4.5	-26	IAEA	IAEA
8/31/1973	GNIP	Rain Water	-3.1	-16	IAEA	IAEA
9/30/1973	GNIP	Rain Water	-5.9	-30	IAEA	IAEA
10/31/1973	GNIP	Rain Water	-2.3	-19	IAEA	IAEA
12/31/1973	GNIP	Rain Water	-1.9	-4	IAEA	IAEA
1/31/1974	GNIP	Rain Water	-5.0	-19	IAEA	IAEA

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
2/28/1974	GNIP	Rain Water	-1.0	-1	IAEA	IAEA
3/31/1974	GNIP	Rain Water	-0.9	-8	IAEA	IAEA
4/30/1974	GNIP	Rain Water	-8.2	-57	IAEA	IAEA
5/31/1974	GNIP	Rain Water	-7.5	-50	IAEA	IAEA
6/30/1974	GNIP	Rain Water	-6.8	-42	IAEA	IAEA
7/31/1974	GNIP	Rain Water	-7.3	-48	IAEA	IAEA
8/31/1974	GNIP	Rain Water	-7.0	-48	IAEA	IAEA
9/30/1974	GNIP	Rain Water	-5.5	-31	IAEA	IAEA
10/31/1974	GNIP	Rain Water	-5.9	-37	IAEA	IAEA
11/30/1974	GNIP	Rain Water	-4.1	-24	IAEA	IAEA
12/31/1974	GNIP	Rain Water	1.6	4	IAEA	IAEA
1/31/1975	GNIP	Rain Water	-1.7	-1	IAEA	IAEA
2/28/1975	GNIP	Rain Water	-0.3	6	IAEA	IAEA
3/31/1975	GNIP	Rain Water	-1.3	3	IAEA	IAEA
4/30/1975	GNIP	Rain Water	-1.2	1	IAEA	IAEA
5/31/1975	GNIP	Rain Water	-3.5	-20	IAEA	IAEA
6/30/1975	GNIP	Rain Water	-2.8	-14	IAEA	IAEA
7/31/1975	GNIP	Rain Water	-4.3	-25	IAEA	IAEA
8/31/1975	GNIP	Rain Water	-7.3	-47	IAEA	IAEA
9/30/1975	GNIP	Rain Water	-6.1	-36	IAEA	IAEA
10/31/1975	GNIP	Rain Water	-5.7	-33	IAEA	IAEA
11/30/1975	GNIP	Rain Water	-5.6	-34	IAEA	IAEA
1/31/1976	GNIP	Rain Water	-3.3	-12	IAEA	IAEA
2/29/1976	GNIP	Rain Water	-3.1	-11	IAEA	IAEA
3/31/1976	GNIP	Rain Water	-2.6	-10	IAEA	IAEA
4/30/1976	GNIP	Rain Water	-2.3	-10	IAEA	IAEA
5/31/1976	GNIP	Rain Water	-5.5	-33	IAEA	IAEA
6/30/1976	GNIP	Rain Water	-5.4	-33	IAEA	IAEA
7/31/1976	GNIP	Rain Water	-8.4	-57	IAEA	IAEA
8/31/1976	GNIP	Rain Water	-8.0	-54	IAEA	IAEA
9/30/1976	GNIP	Rain Water	-4.8	-29	IAEA	IAEA
10/31/1976	GNIP	Rain Water	-2.4	-8	IAEA	IAEA
11/30/1976	GNIP	Rain Water	-3.2	-17	IAEA	IAEA
12/31/1976	GNIP	Rain Water	-3.6	-19	IAEA	IAEA
1/31/1977	GNIP	Rain Water	-3.1	-16	IAEA	IAEA
2/28/1977	GNIP	Rain Water	-0.6	10	IAEA	IAEA
3/31/1977	GNIP	Rain Water	-1.1	6	IAEA	IAEA
2/19/2009	UOG	Rain Water	-1.4	-6	ALPS	SIL CZG
6/11/2009	UOG	Rain Water	-5.1	-33	ALPS	SIL CZG

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
8/20/2009	UOG	Rain Water	-5.4	-37	ALPS	SIL CZG
11/18/2009	UOG	Rain Water	-1.5	2	ALPS	SIL CZG
1/27/2010	UOG	Rain Water	-1.3	0	ALPS	SIL CZG
5/19/2010	UOG	Rain Water	-1.3	-5	ALPS	SIL CZG
9/8/2010	UOG	Rain Water	-7.6	-55	ALPS	SIL CZG
12/15/2010	UOG	Rain Water	-2.6	-9	SIL CZG	SIL CZG
12/29/2010	UOG	Rain Water	-2.2	-6	SIL CZG	SIL CZG
1/12/2011	UOG	Rain Water	-2.6	-11	SIL CZG	SIL CZG
2/9/2011	UOG	Rain Water	-3.9	-21	SIL CZG	SIL CZG
2/23/2011	UOG	Rain Water	-4.0	-5	SIL CZG	SIL CZG
4/6/2011	UOG	Rain Water	-4.8	-29	SIL CZG	SIL CZG
4/20/2011	UOG	Rain Water	-3.9	-22	SIL CZG	SIL CZG
5/4/2011	UOG	Rain Water	-1.9	-7	SIL CZG	SIL CZG
5/18/2011	UOG	Rain Water	-2.1	-7	SIL CZG	SIL CZG
6/1/2011	UOG	Rain Water	-4.2	-24	SIL CZG	SIL CZG
6/15/2011	UOG	Rain Water	-1.8	-6	SIL CZG	SIL CZG
6/29/2011	UOG	Rain Water	-3.2	-17	SIL CZG	SIL CZG
7/13/2011	UOG	Rain Water	-6.7	-45	SIL CZG	SIL CZG
9/2/2011	UOG	Rain Water	-13.1	-90	SIL CZG	SIL CZG
9/2/2011	UOG	Rain Water	-13.0	-90	SIL CZG	SIL CZG
9/2/2011	UOG	Rain Water	-13.0	-90	SIL CZG	SIL CZG
9/16/2011	UOG	Rain Water	-7.6	-50	SIL CZG	SIL CZG
9/30/2011	UOG	Rain Water	-6.2	-36	SIL CZG	SIL CZG
10/14/2011	UOG	Rain Water	-5.6	-34	SIL CZG	SIL CZG
10/28/2011	UOG	Rain Water	-5.8	-37	SIL CZG	SIL CZG
11/25/2011	UOG	Rain Water	-2.6	-11	SIL CZG	SIL CZG
12/9/2011	UOG	Rain Water	-2.5	-12	SIL CZG	SIL CZG
12/23/2011	UOG	Rain Water	-1.4	-3	SIL CZG	SIL CZG
1/6/2012	UOG	Rain Water	-1.3	-1	SIL CZG	SIL CZG
1/20/2012	UOG	Rain Water	-1.2	7	SIL CZG	SIL CZG
2/22/2012	UOG	Rain Water	-1.9	-3	SIL CZG	SIL CZG
3/21/2012	UOG	Rain Water	-1.7	0	SIL CZG	SIL CZG
4/4/2012	UOG	Rain Water	-2.2	-7	SIL CZG	SIL CZG
5/16/2012	UOG	Rain Water	-2.9	-10	SIL CZG	SIL CZG
6/29/2012	UOG	Rain Water	-3.6	-18	SIL CZG	SIL CZG
7/13/2012	UOG	Rain Water	-2.7	-26	SIL CZG	SIL CZG
7/27/2012	UOG	Rain Water	-2.0	-20	SIL CZG	SIL CZG
8/10/2012	UOG	Rain Water	-8.3	-58	SIL CZG	SIL CZG
8/24/2012	UOG	Rain Water	-7.3	-53	SIL CZG	SIL CZG

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
9/21/2012	UOG	Rain Water	-7.0	-45	SIL CZG	SIL CZG
10/5/2012	UOG	Rain Water	-7.7	-52	SIL CZG	SIL CZG
10/19/2012	UOG	Rain Water	-7.1	-47	SIL CZG	SIL CZG
11/2/2012	UOG	Rain Water	-1.2	-9	SIL CZG	SIL CZG
11/16/2012	UOG	Rain Water	-1.6	-9	SIL CZG	SIL CZG
12/28/2012	UOG	Rain Water	-1.8	-5	SIL CZG	SIL CZG
1/25/2013	UOG	Rain Water	-1.4	1	SIL CZG	SIL CZG
2/22/2013	UOG	Rain Water	-1.0	4	SIL CZG	SIL CZG
3/22/2013	UOG	Rain Water	-6.0	-37	SIL CZG	SIL CZG
4/5/2013	UOG	Rain Water	-1.1	-1	SIL CZG	SIL CZG
4/19/2013	UOG	Rain Water	-1.3	3	SIL CZG	SIL CZG
4/19/2013	UOG	Rain Water	-3.9	3	SIL CZG	SIL CZG
5/17/2013	UOG	Rain Water	-3.1	-14	SIL CZG	SIL CZG
5/31/2013	UOG	Rain Water	-1.6	-4	SIL CZG	SIL CZG
6/14/2013	UOG	Rain Water	-2.9	-13	SIL CZG	SIL CZG
6/28/2013	UOG	Rain Water	-2.9	-15	SIL CZG	SIL CZG
7/12/2013	UOG	Rain Water	-3.1	-15	SIL CZG	SIL CZG
7/26/2013	UOG	Rain Water	-3.0	-16	SIL CZG	SIL CZG
8/23/2013	UOG	Rain Water	-3.7	-14	SIL CZG	SIL CZG
9/6/2013	UOG	Rain Water	-5.0	-29	SIL CZG	SIL CZG
9/20/2013	UOG	Rain Water	-9.0	-61	SIL CZG	SIL CZG
9/23/2013	UOG	Rain Water	-8.2	-53	SIL CZG	SIL CZG
10/18/2013	UOG	Rain Water	-9.0	-58	SIL CZG	SIL CZG
11/1/2013	UOG	Rain Water	-4.1	-23	SIL CZG	SIL CZG
11/15/2013	UOG	Rain Water	-2.7	-12	SIL CZG	SIL CZG
12/6/2013	UOG	Rain Water	-1.8	-5	SIL CZG	SIL CZG
12/19/2013	UOG	Rain Water	-2.0	-3	SIL CZG	SIL CZG
1/16/2014	UOG	Rain Water	-1.6	-1	SIL CZG	SIL CZG
1/29/2014	UOG	Rain Water	-6.7	-42	SIL CZG	SIL CZG
2/12/2014	UOG	Rain Water	-4.1	-22	SIL CZG	SIL CZG
2/26/2014	UOG	Rain Water	-2.0	-2	SIL CZG	SIL CZG
3/12/2014	UOG	Rain Water	-3.4	-19	SIL CZG	SIL CZG
3/26/2014	UOG	Rain Water	-1.3	2	SIL CZG	SIL CZG
4/9/2014	UOG	Rain Water	-1.3	-2	SIL CZG	SIL CZG
4/24/2014	UOG	Rain Water	-2.9	-20	SIL CZG	SIL CZG
5/7/2014	UOG	Rain Water	-5.5	-35	SIL CZG	SIL CZG
5/21/2014	UOG	Rain Water	-2.0	-6	SIL CZG	SIL CZG
6/4/2014	UOG	Rain Water	-3.3	-23	SIL CZG	SIL CZG
6/18/2014	UOG	Rain Water	-2.4	-13	SIL CZG	SIL CZG

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
7/2/2014	UOG	Rain Water	-4.0	-20	SIL CZG	SIL CZG
7/16/2014	UOG	Rain Water	-6.0	-44	SIL CZG	SIL CZG
7/31/2014	UOG	Rain Water	-10.9	-79	SIL CZG	SIL CZG
8/15/2014	UOG	Rain Water	-4.1	-32	SIL CZG	SIL CZG
9/19/2014	UOG	Rain Water	-6.0	-32	SIL CZG	SIL CZG
10/10/2014	UOG	Rain Water	-5.2	-67	SIL CZG	SIL CZG
10/24/2014	UOG	Rain Water	-9.3	-30	SIL CZG	SIL CZG
12/2/2014	UOG	Rain Water	-4.3	-4	SIL CZG	SIL CZG
1/9/2015	UOG	Rain Water	-1.5	0	SIL CZG	SIL CZG
1/28/2015	UOG	Rain Water	-2.8	39	SIL CZG	SIL CZG
2/12/2015	UOG	Rain Water	8.8	17	SIL CZG	SIL CZG
2/26/2015	UOG	Rain Water	0.3	-16	SIL CZG	SIL CZG
5/14/2015	UOG	Rain Water	1.1	7	ALPS	ALPS
5/16/2015	UOG	Rain Water	-9.1	-64	ALPS	ALPS
7/10/2015	UOG	Rain Water	-8.1	-62	ALPS	ALPS
8/20/2015	UOG	Rain Water	-6.1	-44	ALPS	ALPS
9/16/2015	UOG	Rain Water	-5.2	-32	ALPS	ALPS
10/20/2015	UOG	Rain Water	-4.6	-27	ALPS	ALPS
10/29/2015	UOG	Rain Water	-4.7	-28	ALPS	ALPS
11/5/2015	UOG	Rain Water	4.8	21	ALPS	ALPS
11/12/2015	UOG	Rain Water	-2.1	-6	ALPS	ALPS
11/19/2015	UOG	Rain Water	-2.6	-10	ALPS	ALPS
11/23/2015	UOG	Rain Water	-6.4	-42	ALPS	ALPS
11/26/2015	UOG	Rain Water	-0.6	1	ALPS	ALPS
12/1/2015	UOG	Rain Water	-0.5	3	ALPS	ALPS
12/3/2015	UOG	Rain Water	0.1	5	ALPS	ALPS
12/17/2015	UOG	Rain Water	1.8	7	ALPS	ALPS
11/6/2013	A10	Well	-6.2	-41	SIL CZG	SIL CZG
1/31/2014	A10	Well	-6.3	-44	SIL CZG	SIL CZG
5/8/2014	A10	Well	-6.3	-43	SIL CZG	SIL CZG
8/14/2014	A10	Well	-6.2	-40	SIL CZG	SIL CZG
10/23/2014	A10	Well		-39		SIL CZG
11/6/2013	AG2A	Well	-6.6	-42	SIL CZG	SIL CZG
5/8/2014	AG2A	Well	-6.3	-42	SIL CZG	SIL CZG
8/14/2014	AG2A	Well	-6.5	-44	SIL CZG	SIL CZG
10/23/2014	AG2A	Well	-6.3	-40	SIL CZG	SIL CZG
11/6/2013	D14	Well	-5.9	-38	SIL CZG	SIL CZG
1/31/2014	D14	Well	-5.9	-39	SIL CZG	SIL CZG
5/8/2014	D14	Well	-5.9		SIL CZG	

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Sample Date [a]	Site Name (Replicate*)	Site Type	$\delta^{18}O$ (‰ VSMOW)	δD (‰ VSMOW)	Lab ($\delta^{18}O$)	Lab (δD)
8/14/2014	D14	Well	-6.1		SIL CZG	
11/6/2013	F02	Well	-6.3	-41	SIL CZG	SIL CZG
1/31/2014	F02	Well	-6.3	-40	SIL CZG	SIL CZG
5/8/2014	F02	Well	-6.2	-41	SIL CZG	SIL CZG
8/14/2014	F02	Well	-6.1	-39	SIL CZG	SIL CZG
11/6/2013	M04	Well	-6.2	-40	SIL CZG	SIL CZG
1/31/2014	M04	Well	-6.3	-40	SIL CZG	SIL CZG
8/14/2014	M04	Well	-6.2	-40	SIL CZG	SIL CZG
10/23/2014	M04	Well		-40		SIL CZG
11/6/2013	M18	Well	-6.1	-37	SIL CZG	SIL CZG
1/31/2014	M18	Well	-5.8	-39	SIL CZG	SIL CZG
5/8/2014	M18	Well	-6.0	-38	SIL CZG	SIL CZG
8/14/2014	M18	Well	-6.0	-39	SIL CZG	SIL CZG
11/6/2013	Y02	Well	-6.2	-40	SIL CZG	SIL CZG
1/31/2014	Y02	Well	-6.1	-42	SIL CZG	SIL CZG
5/8/2014	Y02	Well	-6.1	-38	SIL CZG	SIL CZG
8/14/2014	Y02	Well	-6.1	-41	SIL CZG	SIL CZG
10/23/2014	Y02	Well		-43		SIL CZG
11/6/2013	Y07	Well	-6.2	-39	SIL CZG	SIL CZG
1/31/2014	Y07	Well	-6.3	-42	SIL CZG	SIL CZG
5/8/2014	Y07	Well	-6.2	-40	SIL CZG	SIL CZG
8/14/2014	Y07	Well	-6.3	-40	SIL CZG	SIL CZG
10/23/2014	Y07	Well		-39		SIL CZG
11/6/2013	Y15	Well	-6.3	-40	SIL CZG	SIL CZG
1/31/2014	Y15	Well	-6.2	-40	SIL CZG	SIL CZG
5/8/2014	Y15	Well	-6.2	-40	SIL CZG	SIL CZG
8/14/2014	Y15	Well	-6.3	-40	SIL CZG	SIL CZG
10/23/2014	Y15	Well		-41		SIL CZG
11/6/2013	Y23	Well	-6.4	-41	SIL CZG	SIL CZG
1/31/2014	Y23	Well	-6.2	-40	SIL CZG	SIL CZG
5/8/2014	Y23	Well	-6.3	-39	SIL CZG	SIL CZG
8/14/2014	Y23	Well	-6.2	-38	SIL CZG	SIL CZG
10/23/2014	Y23	Well		-38		SIL CZG

[a] Cave dripwater stable isotope data from 07/2008 to 11/2010 obtained from Partin et al. (2012).

ALPS - Analytic Lab for Paleoclimate Studies; SIL CZG - Stable Isotope Lab for Critical Zone Gases, UOC - University of Copenhagen; IAEA - International Atomic Energy Agency.

Table S1.4 Average cave drip rate through the study period.

Date Collected [a, b]	**Site Name**	**Average Drip/Minute**
9/22/2008	FTM	4.3
10/20/2008	FTM	5.0
11/17/2008	FTM	5.5
12/15/2008	FTM	2.5
1/12/2009	FTM	4.3
2/17/2009	FTM	15.0
3/16/2009	FTM	3.0
4/13/2009	FTM	2.6
5/12/2009	FTM	2.5
6/11/2009	FTM	2.5
7/14/2009	FTM	2.2
8/21/2009	FTM	6.2
9/21/2009	FTM	5.5
10/19/2009	FTM	5.5
11/23/2009	FTM	5.3
12/21/2009	FTM	5.3
1/25/2010	FTM	5.2
3/1/2010	FTM	5.2
4/5/2010	FTM	4.4
5/3/2010	FTM	3.5
6/7/2010	FTM	2.8
7/12/2010	FTM	2.5
8/16/2010	FTM	2.5
9/27/2010	FTM	2.3
10/25/2010	FTM	2.1
11/22/2010	FTM	5.5
12/20/2010	FTM	4.5
1/24/2011	FTM	3.5
2/21/2011	FTM	4.0
3/28/2011	FTM	4.4
3/29/2011	FTM	4.3

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Date Collected [a, b]	Site Name	Average Drip/Minute
4/25/2011	FTM	4.6
5/23/2011	FTM	5.2
6/20/2011	FTM	4.2
7/18/2011	FTM	3.3
8/29/2011	FTM	5.5
9/26/2011	FTM	5.5
10/24/2011	FTM	5.6
11/21/2011	FTM	6.0
12/19/2011	FTM	5.5
1/23/2012	FTM	5.2
2/27/2012	FTM	4.6
3/26/2012	FTM	3.8
4/24/2012	FTM	3.3
5/21/2012	FTM	3.0
6/28/2012	FTM	2.5
8/2/2012	FTM	2.4
8/3/2012	FTM	2.4
8/27/2012	FTM	3.5
9/24/2012	FTM	5.0
10/22/2012	FTM	5.5
11/19/2012	FTM	5.5
12/21/2012	FTM	5.0
1/15/2013	FTM	3.8
2/18/2013	FTM	3.3
3/18/2013	FTM	2.9
4/22/2013	FTM	2.5
5/20/2013	FTM	2.3
6/25/2013	FTM	2.2
7/29/2013	FTM	2.2
8/26/2013	FTM	1.7
9/23/2013	FTM	5.5
10/21/2013	FTM	5.7
11/18/2013	FTM	4.9
12/16/2013	FTM	5.0
1/21/2014	FTM	4.1
1/22/2014	FTM	4.3
2/17/2014	FTM	5.2

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Date Collected [a, b]	Site Name	Average Drip/Minute
2/18/2014	FTM	5.0
3/17/2014	FTM	5.3
3/18/2014	FTM	5.3
4/22/2014	FTM	3.7
4/23/2014	FTM	3.7
5/22/2014	FTM	3.0
5/23/2014	FTM	3.0
6/16/2014	FTM	2.6
6/17/2014	FTM	2.5
8/12/2014	FTM	5.0
8/18/2014	FTM	5.2
9/22/2014	FTM	5.0
9/23/2014	FTM	5.2
10/30/2014	FTM	5.0
10/31/2014	FTM	5.0
11/28/2014	FTM	5.5
11/29/2014	FTM	5.6
12/29/2014	FTM	5.3
12/30/2014	FTM	5.3
1/30/2015	FTM	4.3
1/31/2015	FTM	4.3
2/27/2015	FTM	4.7
2/28/2015	FTM	4.6
3/27/2015	FTM	3.8
3/28/2015	FTM	3.8
5/1/2015	FTM	3.2
5/29/2015	FTM	4.6
6/25/2015	FTM	4.5
7/29/2015	FTM	5.0
8/31/2015	FTM	5.3
9/28/2015	FTM	5.5
10/26/2015	FTM	5.8
11/23/2015	FTM	4.0
12/21/2015	FTM	5.5
12/17/2013	FTM	5.0
9/28/2010	FTM	2.2
10/25/2011	FTM	5.6

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Date Collected [a, b]	Site Name	Average Drip/Minute
7/15/2009	FTM	2.2
9/23/2008	FTM	5.5
9/27/2011	FTM	5.5
6/29/2012	FTM	2.5
5/13/2009	FTM	2.5
8/17/2010	FTM	2.5
11/22/2011	FTM	6.0
9/24/2013	FTM	5.0
12/20/2011	FTM	5.5
8/22/2009	FTM	6.0
6/26/2013	FTM	2.2
3/2/2010	FTM	5.2
11/24/2009	FTM	5.3
10/22/2013	FTM	5.0
7/30/2013	FTM	2.2
7/13/2010	FTM	2.5
5/4/2010	FTM	3.5
5/22/2012	FTM	3.0
12/16/2008	FTM	2.4
10/26/2010	FTM	2.1
8/27/2013	FTM	1.7
10/21/2009	FTM	5.5
2/22/2011	FTM	4.0
1/26/2010	FTM	5.2
9/22/2009	FTM	5.5
11/23/2010	FTM	5.5
3/19/2013	FTM	2.9
4/6/2010	FTM	4.4
11/18/2008	FTM	5.0
6/21/2011	FTM	4.2
1/24/2012	FTM	5.0
5/21/2013	FTM	2.3
4/23/2013	FTM	2.5
12/21/2010	FTM	4.3
8/28/2012	FTM	4.3
1/13/2009	FTM	4.3
11/19/2013	FTM	4.2

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Date Collected [a, b]	Site Name	Average Drip/Minute
1/25/2011	FTM	3.5
4/26/2011	FTM	4.6
11/20/2012	FTM	5.5
10/23/2012	FTM	5.5
9/25/2012	FTM	5.0
3/17/2009	FTM	3.1
8/30/2011	FTM	5.5
12/22/2009	FTM	5.3
6/8/2010	FTM	2.8
1/16/2013	FTM	3.8
2/28/2012	FTM	4.6
4/23/2012	FTM	3.2
4/14/2009	FTM	2.4
2/18/2009	FTM	4.0
3/27/2012	FTM	3.8
5/24/2011	FTM	5.2
7/19/2011	FTM	3.3
2/27/2015	SMP	0.2
2/28/2015	SMP	0.2
3/27/2015	SMP	0.2
3/28/2015	SMP	0.2
5/1/2015	SMP	0.1
6/25/2015	SMP	0.2
10/26/2015	SMP	0.2
11/23/2015	SMP	0.1
12/21/2015	SMP	0.2
9/22/2008	ST1	1.4
10/20/2008	ST1	1.4
11/17/2008	ST1	1.4
12/15/2008	ST1	1.2
1/12/2009	ST1	0.3
2/17/2009	ST1	0.0
3/16/2009	ST1	1.2
3/17/2009	ST1	0.7
4/13/2009	ST1	0.6
5/12/2009	ST1	0.8
6/11/2009	ST1	0.5

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Date Collected [a, b]	Site Name	Average Drip/Minute
7/14/2009	ST1	0.4
8/21/2009	ST1	1.0
9/21/2009	ST1	2.0
10/19/2009	ST1	1.7
11/23/2009	ST1	1.6
12/21/2009	ST1	1.9
1/25/2010	ST1	1.6
2/1/2010	ST1	0.0
2/1/2010	ST1	0.0
3/1/2010	ST1	1.4
4/5/2010	ST1	0.0
4/6/2010	ST1	0.0
5/3/2010	ST1	0.0
6/7/2010	ST1	0.5
7/12/2010	ST1	0.5
8/16/2010	ST1	0.6
9/27/2010	ST1	0.4
10/25/2010	ST1	1.4
11/22/2010	ST1	1.6
12/20/2010	ST1	1.2
1/24/2011	ST1	0.4
2/21/2011	ST1	1.6
3/28/2011	ST1	0.8
4/25/2011	ST1	0.2
5/23/2011	ST1	0.9
6/20/2011	ST1	0.6
7/18/2011	ST1	0.6
8/29/2011	ST1	2.1
9/26/2011	ST1	3.2
10/24/2011	ST1	1.4
11/21/2011	ST1	0.8
12/19/2011	ST1	1.4
1/23/2012	ST1	1.3
2/27/2012	ST1	0.8
3/26/2012	ST1	0.1
4/23/2012	ST1	0.0
4/24/2012	ST1	0.0

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Date Collected [a, b]	Site Name	Average Drip/Minute
5/21/2012	ST1	0.0
6/28/2012	ST1	0.0
6/29/2012	ST1	0.0
8/2/2012	ST1	0.0
8/3/2012	ST1	0.0
8/27/2012	ST1	1.4
9/24/2012	ST1	1.1
10/22/2012	ST1	1.2
11/19/2012	ST1	0.7
12/21/2012	ST1	0.0
1/15/2013	ST1	0.0
1/16/2013	ST1	0.0
2/18/2013	ST1	0.0
2/19/2013	ST1	0.0
3/18/2013	ST1	0.0
4/22/2013	ST1	0.0
4/23/2013	ST1	0.0
5/20/2013	ST1	0.0
3/29/2011	ST1	1.1
6/25/2013	ST1	0.0
7/29/2013	ST1	0.0
8/26/2013	ST1	0.0
8/27/2013	ST1	0.0
9/23/2013	ST1	0.0
10/21/2013	ST1	1.5
11/18/2013	ST1	1.4
12/16/2013	ST1	0.7
1/22/2014	ST1	0.6
2/18/2014	ST1	0.5
3/17/2014	ST1	0.5
4/22/2014	ST1	0.1
4/23/2014	ST1	0.1
5/22/2014	ST1	0.0
7/19/2011	ST1	0.6
5/23/2014	ST1	0.0
6/16/2014	ST1	0.0
8/12/2014	ST1	1.1

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Date Collected [a, b]	Site Name	Average Drip/Minute
8/30/2011	ST1	2.0
9/22/2014	ST1	1.0
9/23/2014	ST1	0.8
10/30/2014	ST1	1.0
11/28/2014	ST1	0.7
9/22/2009	ST1	2.0
12/29/2014	ST1	0.8
8/22/2009	ST1	1.2
1/30/2015	ST1	1.0
2/27/2015	ST1	0.8
8/28/2012	ST1	1.2
10/26/2010	ST1	1.2
9/28/2010	ST1	0.4
2/28/2015	ST1	0.8
10/21/2009	ST1	1.6
3/27/2015	ST1	0.5
5/1/2015	ST1	0.3
1/25/2011	ST1	0.5
10/21/2008	ST1	1.4
5/29/2015	ST1	1.1
12/22/2009	ST1	1.9
9/27/2011	ST1	3.0
9/25/2012	ST1	1.4
11/24/2009	ST1	1.7
6/25/2015	ST1	0.6
11/18/2008	ST1	1.4
9/23/2008	ST1	1.3
5/13/2009	ST1	0.9
11/23/2010	ST1	1.4
4/26/2011	ST1	0.4
7/29/2015	ST1	1.2
12/20/2011	ST1	1.3
2/22/2011	ST1	1.5
11/22/2011	ST1	0.8
6/21/2011	ST1	0.5
1/26/2010	ST1	1.6
8/31/2015	ST1	0.6

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Date Collected [a, b]	Site Name	Average Drip/Minute
12/16/2008	ST1	0.8
9/28/2015	ST1	1.0
10/25/2011	ST1	1.3
10/23/2012	ST1	1.1
5/24/2011	ST1	1.2
10/26/2015	ST1	0.8
4/14/2009	ST1	0.6
6/12/2009	ST1	0.0
1/24/2012	ST1	1.3
5/4/2010	ST1	0.5
7/13/2010	ST1	0.6
7/15/2009	ST1	0.6
11/23/2015	ST1	0.7
6/8/2010	ST1	0.3
12/21/2015	ST1	1.0
11/20/2012	ST1	0.8
5/22/2012	ST1	0.0
3/27/2012	ST1	0.1
3/2/2010	ST1	1.2
2/18/2009	ST1	0.0
1/13/2009	ST1	0.2
8/17/2010	ST1	0.6
3/28/2015	ST1	0.4
12/21/2010	ST1	1.6
9/24/2013	ST1	1.0
7/30/2013	ST1	0.0
3/19/2013	ST1	0.0
2/28/2012	ST1	0.8
12/22/2012	ST1	0.5
8/18/2014	ST1	0.9
6/17/2014	ST1	0.0
3/18/2014	ST1	0.5
10/22/2013	ST1	1.4
6/26/2013	ST1	0.0
12/30/2014	ST1	0.6
10/31/2014	ST1	1.0
11/19/2013	ST1	1.4

e 1. c n in ed

Date Collected [a, b]	Site Name	Average Drip/Minute
1/21/2014	ST1	0.0
2/17/2014	ST1	0.7
1/31/2015	ST1	1.1
11/29/2014	ST1	0.6
5/21/2013	ST1	0.0
12/17/2013	ST1	0.8
9/22/2008	ST2	2.0
10/20/2008	ST2	1.8
11/17/2008	ST2	1.5
12/15/2008	ST2	1.4
1/12/2009	ST2	1.3
2/17/2009	ST2	1.2
3/16/2009	ST2	1.1
4/13/2009	ST2	0.8
5/12/2009	ST2	0.8
6/11/2009	ST2	0.7
7/14/2009	ST2	0.8
8/21/2009	ST2	1.0
9/21/2009	ST2	1.3
10/19/2009	ST2	1.2
11/23/2009	ST2	1.0
12/21/2009	ST2	1.0
1/25/2010	ST2	1.0
3/1/2010	ST2	0.8
4/5/2010	ST2	0.8
5/3/2010	ST2	0.7
6/7/2010	ST2	0.7
7/12/2010	ST2	0.7
8/16/2010	ST2	0.7
9/27/2010	ST2	0.7
10/25/2010	ST2	0.7
11/22/2010	ST2	0.5
12/20/2010	ST2	0.9
1/24/2011	ST2	0.7
2/21/2011	ST2	0.8
3/28/2011	ST2	0.8
4/25/2011	ST2	0.8

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Date Collected [a, b]	Site Name	Average Drip/Minute
5/23/2011	ST2	0.8
6/20/2011	ST2	0.7
7/18/2011	ST2	0.7
8/29/2011	ST2	0.9
9/26/2011	ST2	0.9
10/24/2011	ST2	0.9
10/25/2011	ST2	0.9
11/21/2011	ST2	0.9
11/22/2011	ST2	0.9
12/19/2011	ST2	0.8
1/23/2012	ST2	0.7
2/27/2012	ST2	0.7
2/28/2012	ST2	0.7
3/26/2012	ST2	0.6
3/27/2012	ST2	0.6
4/23/2012	ST2	0.6
4/24/2012	ST2	0.6
5/21/2012	ST2	0.6
5/22/2012	ST2	0.6
6/28/2012	ST2	0.5
6/29/2012	ST2	0.5
8/2/2012	ST2	0.5
8/27/2012	ST2	0.6
9/24/2012	ST2	0.7
10/22/2012	ST2	0.8
11/19/2012	ST2	0.6
12/21/2012	ST2	0.6
1/15/2013	ST2	0.5
2/18/2013	ST2	0.5
2/19/2013	ST2	0.5
3/18/2013	ST2	0.5
4/22/2013	ST2	0.5
5/20/2013	ST2	0.4
6/25/2013	ST2	0.4
7/29/2013	ST2	0.4
12/20/2011	ST2	0.7
12/16/2008	ST2	1.4

e 1. c n in ed

Date Collected [a, b]	Site Name	Average Drip/Minute
1/25/2011	ST2	0.8
11/18/2008	ST2	1.4
6/21/2011	ST2	0.7
5/24/2011	ST2	0.8
8/22/2009	ST2	1.0
8/30/2011	ST2	0.9
1/13/2009	ST2	1.2
9/23/2008	ST2	2.1
7/13/2010	ST2	0.7
2/18/2009	ST2	1.1
5/13/2009	ST2	0.8
10/26/2010	ST2	0.7
9/28/2010	ST2	0.7
11/23/2010	ST2	1.0
4/26/2011	ST2	0.7
10/21/2009	ST2	1.2
4/6/2010	ST2	0.7
9/22/2009	ST2	1.3
3/2/2010	ST2	0.8
8/17/2010	ST2	0.7
12/21/2010	ST2	0.9
9/27/2011	ST2	0.9
2/22/2011	ST2	0.8
11/24/2009	ST2	1.0
3/17/2009	ST2	1.1
5/4/2010	ST2	0.8
8/28/2012	ST2	0.7
1/26/2010	ST2	1.0
4/14/2009	ST2	0.8
10/23/2012	ST2	0.7
7/15/2009	ST2	0.8
6/8/2010	ST2	0.7
9/25/2012	ST2	0.7
4/23/2013	ST2	0.4
1/24/2012	ST2	0.7
5/21/2013	ST2	0.4
12/22/2009	ST2	1.0

e 1. c n in ed

Date Collected [a, b]	Site Name	Average Drip/Minute
6/26/2013	ST2	0.4
11/20/2012	ST2	0.6
3/19/2013	ST2	0.5
8/3/2012	ST2	0.5
12/22/2012	ST2	0.6
7/19/2011	ST2	0.7
3/29/2011	ST2	0.8
10/21/2008	ST2	1.8
1/16/2013	ST2	0.4
7/30/2013	ST2	0.4
8/27/2013	ST2	0.4
9/24/2013	ST2	0.5
10/22/2013	ST2	0.7
11/19/2013	ST2	0.8
12/17/2013	ST2	0.7
1/21/2014	ST2	0.6
2/17/2014	ST2	0.8
4/23/2014	ST2	0.6
5/23/2014	ST2	0.5
8/18/2014	ST2	0.7
9/23/2014	ST2	0.6
10/31/2014	ST2	0.6
8/26/2013	ST2	0.4
9/23/2013	ST2	0.4
10/21/2013	ST2	0.8
11/18/2013	ST2	0.8
12/16/2013	ST2	0.7
1/22/2014	ST2	0.6
2/18/2014	ST2	0.7
3/17/2014	ST2	0.7
3/18/2014	ST2	0.6
4/22/2014	ST2	0.6
5/22/2014	ST2	0.6
6/16/2014	ST2	0.5
6/17/2014	ST2	0.5
8/12/2014	ST2	0.3
9/22/2014	ST2	0.7

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Date Collected [a, b]	Site Name	Average Drip/Minute
10/30/2014	ST2	0.6
11/28/2014	ST2	0.6
11/29/2014	ST2	0.6
12/29/2014	ST2	0.5
12/30/2014	ST2	0.5
1/30/2015	ST2	0.6
1/31/2015	ST2	0.6
2/27/2015	ST2	0.6
2/28/2015	ST2	0.6
3/27/2015	ST2	0.5
3/28/2015	ST2	0.5
5/1/2015	ST2	0.5
5/29/2015	ST2	0.6
6/25/2015	ST2	0.6
7/29/2015	ST2	0.5
8/31/2015	ST2	0.6
9/28/2015	ST2	0.7
10/26/2015	ST2	0.7
11/23/2015	ST2	0.6
12/21/2015	ST2	0.6
9/22/2008	TRN	44.0
9/23/2008	TRN	50.0
10/20/2008	TRN	49.3
10/21/2008	TRN	47.3
11/17/2008	TRN	46.0
11/18/2008	TRN	46.0
12/15/2008	TRN	41.3
12/16/2008	TRN	39.3
1/12/2009	TRN	102.0
1/13/2009	TRN	100.0
2/17/2009	TRN	84.7
2/18/2009	TRN	80.0
3/16/2009	TRN	72.0
3/17/2009	TRN	74.7
4/13/2009	TRN	66.0
4/14/2009	TRN	66.7
5/12/2009	TRN	64.0

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Date Collected [a, b]	Site Name	Average Drip/Minute
5/13/2009	TRN	68.0
6/11/2009	TRN	58.7
7/14/2009	TRN	53.3
7/15/2009	TRN	51.3
8/21/2009	TRN	46.0
8/22/2009	TRN	42.7
9/21/2009	TRN	92.7
9/22/2009	TRN	90.0
10/19/2009	TRN	153.3
10/21/2009	TRN	158.0
11/23/2009	TRN	147.3
11/24/2009	TRN	152.0
12/21/2009	TRN	114.7
12/22/2009	TRN	115.3
1/25/2010	TRN	109.3
1/26/2010	TRN	109.3
3/1/2010	TRN	100.0
3/2/2010	TRN	102.0
4/5/2010	TRN	94.7
5/3/2010	TRN	92.7
5/4/2010	TRN	94.7
6/7/2010	TRN	80.7
6/8/2010	TRN	80.0
7/12/2010	TRN	68.0
7/13/2010	TRN	70.0
8/16/2010	TRN	67.3
8/17/2010	TRN	66.7
9/27/2010	TRN	58.0
9/28/2010	TRN	53.3
10/25/2010	TRN	50.0
10/26/2010	TRN	46.7
11/22/2010	TRN	43.3
11/23/2010	TRN	42.0
12/20/2010	TRN	44.0
12/21/2010	TRN	45.3
1/24/2011	TRN	44.0
1/25/2011	TRN	46.0

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Date Collected [a, b]	Site Name	Average Drip/Minute
2/21/2011	TRN	46.0
2/22/2011	TRN	48.0
3/28/2011	TRN	46.0
3/29/2011	TRN	47.3
4/25/2011	TRN	48.0
4/26/2011	TRN	50.0
5/23/2011	TRN	54.0
5/24/2011	TRN	56.0
6/20/2011	TRN	58.0
6/21/2011	TRN	56.0
7/18/2011	TRN	56.7
7/19/2011	TRN	56.0
8/29/2011	TRN	46.0
8/30/2011	TRN	49.3
9/26/2011	TRN	210.0
9/27/2011	TRN	144.0
10/24/2011	TRN	154.3
10/25/2011	TRN	151.0
11/21/2011	TRN	173.3
11/22/2011	TRN	174.0
12/19/2011	TRN	148.7
12/20/2011	TRN	112.7
1/23/2012	TRN	95.3
1/24/2012	TRN	95.3
2/27/2012	TRN	89.3
2/28/2012	TRN	88.7
3/26/2012	TRN	85.3
3/27/2012	TRN	88.0
4/23/2012	TRN	84.0
4/24/2012	TRN	84.0
5/21/2012	TRN	75.3
5/22/2012	TRN	79.3
6/28/2012	TRN	65.3
6/29/2012	TRN	67.3
8/2/2012	TRN	60.0
8/3/2012	TRN	58.7
8/27/2012	TRN	48.0

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Date Collected [a, b]	Site Name	Average Drip/Minute
8/28/2012	TRN	48.7
9/24/2012	TRN	90.0
9/25/2012	TRN	90.0
10/22/2012	TRN	143.3
10/23/2012	TRN	156.0
11/19/2012	TRN	124.7
11/20/2012	TRN	125.3
12/21/2012	TRN	114.0
12/22/2012	TRN	116.7
1/15/2013	TRN	99.3
1/16/2013	TRN	98.0
2/18/2013	TRN	82.7
3/18/2013	TRN	68.7
3/19/2013	TRN	70.7
4/22/2013	TRN	64.7
4/23/2013	TRN	62.7
5/20/2013	TRN	61.3
5/21/2013	TRN	62.7
6/25/2013	TRN	55.3
6/26/2013	TRN	54.7
7/29/2013	TRN	44.7
7/30/2013	TRN	45.3
8/26/2013	TRN	39.3
8/27/2013	TRN	38.0
9/23/2013	TRN	38.0
9/24/2013	TRN	42.0
10/21/2013	TRN	193.3
10/22/2013	TRN	196.0
11/18/2013	TRN	108.7
11/19/2013	TRN	106.7
12/16/2013	TRN	108.7
12/17/2013	TRN	106.7
1/21/2014	TRN	105.3
1/22/2014	TRN	106.0
2/17/2014	TRN	160.7
2/18/2014	TRN	148.0
3/17/2014	TRN	100.7

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Date Collected [a, b]	Site Name	Average Drip/Minute
3/18/2014	TRN	100.7
4/22/2014	TRN	91.3
4/23/2014	TRN	91.3
5/22/2014	TRN	94.7
5/23/2014	TRN	93.3
6/16/2014	TRN	90.7
6/17/2014	TRN	89.3
8/12/2014	TRN	166.0
8/18/2014	TRN	135.3
9/22/2014	TRN	128.0
9/23/2014	TRN	140.0
10/30/2014	TRN	104.0
11/28/2014	TRN	106.0
11/29/2014	TRN	105.3
12/29/2014	TRN	99.3
12/30/2014	TRN	104.7
1/30/2015	TRN	102.0
1/31/2015	TRN	105.3
2/27/2015	TRN	97.3
2/28/2015	TRN	100.0
3/27/2015	TRN	93.3
3/28/2015	TRN	96.7
5/1/2015	TRN	93.3
5/30/2015	TRN	72.7
6/26/2015	TRN	80.0
7/29/2015	TRN	135.3
8/31/2015	TRN	137.3
9/28/2015	TRN	116.0
10/26/2015	TRN	130.0
11/23/2015	TRN	124.0
12/21/2015	TRN	108.0

[a, b] Cave drip rate data from 07/2008 to 11/2010 obtained from Partin et al. (2012) and Noronha et al. (2016), and data from 11/2010 to 07/2016 obtained from Noronha et al. (2016).

Table S1.5 Groundwater, seawater, and soil and saprolite leachate $^{87}Sr/^{86}Sr$ values

Site Name	Type	$^{87}Sr/^{86}Sr$	Lab
Mataguac Saprolite	Saprolite	0.70897	DGS TIMS
MSR-Saprolite	Saprolite	0.70937	DGS TIMS
A-13 Soil	Soil	0.70910	DGS TIMS
D-14 Soil	Soil	0.70911	DGS TIMS
EX-11 Soil	Soil	0.70909	DGS TIMS
M-14 Soil	Soil	0.70901	DGS TIMS
Mataguac Soil	Soil	0.70908	DGS TIMS
MSR-Soil	Soil	0.70872	DGS TIMS
Pagat Soil	Soil	0.70916	DGS TIMS
Y-15 Soil	Soil	0.70917	DGS TIMS
Ritidian Point soils	Soil	0.70916	DGS TIMS
Interior soils	Soil	0.70911	DGS TIMS
A03	Well	0.70900	DGS TIMS
D04	Well	0.70901	DGS TIMS
D10	Well	0.70898	DGS TIMS
D14	Well	0.70905	DGS TIMS
M03	Well	0.70899	DGS TIMS
M06	Well	0.70905	DGS TIMS
M14	Well	0.70908	DGS TIMS
A10	Well	0.70913	DGS TIMS
A10	Well	0.70913	DGS TIMS
A03	Well	0.70900	DGS TIMS
D10	Well	0.70897	DGS TIMS
D14	Well	0.70905	DGS TIMS
D04	Well	0.70901	DGS TIMS
M14	Well	0.70908	DGS TIMS
M03	Well	0.70899	DGS TIMS
M06	Well	0.70905	DGS TIMS
A10	Well	0.70911	DGS TIMS
D14	Well	0.70903	DGS TIMS
F02	Well	0.70900	DGS TIMS
M01	Well	0.70908	DGS TIMS
M04	Well	0.70904	DGS TIMS
Y02	Well	0.70895	DGS TIMS
Y07	Well	0.70894	DGS TIMS
Y15	Well	0.70894	DGS TIMS
Y23	Well	0.70893	DGS TIMS

DGS TIMS - Department of Geological Science Thermal Ionization Mass Spectrometry lab

Table S1.6 Pearson Correlation Coefficients and p-values for correlations between time and cave dripwater $\delta^{18}O$ values and Na^{2+} concentrations

Parameter	**Site**	**Site Type**	**r**	**p-value**	**n**
$\delta^{18}O$	FTM	Dripwater	-0.91	3.95E-10	24
$\delta^{18}O$	SMP	Dripwater	-0.03	0.862	28
$\delta^{18}O$	ST1	Dripwater	-0.69	4.24E-05	28
$\delta^{18}O$	ST2	Dripwater	-0.75	1.63E-05	25
Na^{2+}	FTM	Dripwater	-0.66	1.73E-08	58
Na^{2+}	SMP	Dripwater	-0.86	1.48E-19	64
Na^{2+}	ST1	Dripwater	-0.86	5.25E-25	81
Na^{2+}	ST2	Dripwater	-0.95	5.68E-31	62
Na^{2+}	TRN	Dripwater	-0.73	2.24E-14	79
Na^{2+}	AG2A	Well	-0.96	0.011	4
Na^{2+}	MO4	Well	-0.85	0.032	4
Na^{2+}	Y02	Well	-0.83	0.040	4
Na^{2+}	Y23	Well	-0.96	0.002	4

Appendix II (Chapter II) Supplementary Material

Table S2.1 Municipal (supply and waste) water, and stream and spring water cation concentrations.

Site Type	Site Name	Collection Date	Sr (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Lab
Municipal Waste Water	CoA WWTP	6/14/2013	0.16	15	16	50	20	ICP-Q-MS (UT DGS)
Municipal Waste Water	CoA WWTP	6/15/2013	0.18	27	17	54	16	ICP-Q-MS (UT DGS)
Municipal Waste Water	CoA WWTP	6/17/2013	0.4	24	20	60	14	ICP-Q-MS (UT DGS)
Municipal Waste Water	CoA WWTP	6/18/2013	0.15	25	16	63	18	ICP-Q-MS (UT DGS)
Municipal Waste Water	CoA WWTP	6/20/2013	0.16	37	21	55	0	ICP-Q-MS (UT DGS)
Municipal Waste Water	CoA WWTP	6/21/2013	0.15	23	20	43	14	ICP-Q-MS (UT DGS)
Municipal Waste Water	CoA WWTP	6/22/2013	0.13	24	16	105	26	ICP-Q-MS (UT DGS)
Municipal Waste Water	CoA WWTP	4/30/2011	0.12	31	18	62	14	LCRA
Municipal Waste Water	CoA WWTP	5/1/2011	0.2	34	17	85	12	LCRA
Municipal Supply Water	CLB	6/21/2013	0.12	11	16	27	4.7	ICP-Q-MS (UT DGS)
Municipal Supply Water	SBK	7/25/2012	0.11	11	15	25	3.9	ICP-Q-MS (UT DGS)
Municipal Supply Water	SBK	7/27/2012	0.13	11	14	24	4.2	ICP-Q-MS (UT DGS)

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Site Type	Site Name	Collection Date	Sr (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Lab
Municipal Supply Water	SBK	8/10/2012	0.12	12	18	31	4.9	ICP-Q-MS (UT DGS)
Municipal Supply Water	SBK	9/25/2012	0.12	11	18	28	4.4	ICP-Q-MS (UT DGS)
Municipal Supply Water	TCB	8/28/2010	0.11	11	15	18	3.2	LCRA
Municipal Supply Water	TCB	4/15/2011	0.11	12	16	18	3.6	LCRA
Rural Spring	FK	8/23/2010	0.77	101	17	9	0.6	LCRA
Rural Spring	FK	4/12/2011	0.77	98	16	9	0.5	LCRA
Rural Spring	LN	8/24/2010	0.44	97	16	9	0.5	LCRA
Rural Spring	LN	4/12/2011	0.45	104	17	11	0.6	LCRA
Rural Spring	LR	8/28/2010	0.26	104	20	9	0.7	LCRA
Rural Spring	LR	4/12/2011	0.24	100	19	10	0.8	LCRA
Rural Tributary	ED	7/24/2012	2.5	97	26	10	1.2	ICP-Q-MS (UT DGS)
Rural Tributary	ED	7/27/2012	2.6	94	25	10	1.2	ICP-Q-MS (UT DGS)
Rural Tributary	EM	7/24/2012	1.2	95	19	7	0.9	ICP-Q-MS (UT DGS)
Rural Tributary	EM	7/27/2012	1.3	98	23	8	0.9	ICP-Q-MS (UT DGS)
Rural Tributary	EN	7/24/2012	1.2	85	19	8	1.3	ICP-Q-MS (UT DGS)
Rural Tributary	EN	7/27/2012	1.4	90	20	8	1.3	ICP-Q-MS (UT DGS)

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Site Type	Site Name	Collection Date	Sr (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Lab
Rural Tributary	PN	3/7/2013	0.75	90	16	9	0.5	ICP-Q-MS (UT DGS)
Rural Tributary	PN	6/21/2013	0.8	94	17	9	0.5	ICP-Q-MS (UT DGS)
Urban Spring	BW	8/29/2010	4.9	130	25	33	1.8	LCRA
Urban Spring	BW	4/12/2011	4.1	130	23	34	1.4	LCRA
Urban Spring	FY	8/29/2010	0.25	119	12	12	0.9	LCRA
Urban Spring	FY	4/15/2011	0.23	105	11	11	1	LCRA
Urban Spring	SH	8/24/2010	0.19	166	24	41	1.6	LCRA
Urban Spring	SH	4/12/2011	0.17	160	22	41	1.3	LCRA
Urban Spring	TB	8/29/2010	0.44	138	26	18	1	LCRA
Urban Spring	TB	4/12/2011	0.53	137	29	18	1	LCRA
Urban Spring	TF	8/24/2010	0.7	105	16	19	0.7	LCRA
Urban Spring	TF	4/12/2011	0.73	117	16	15	0.4	LCRA
Urban Spring	TL	8/28/2010	0.27	140	21	23	2.7	LCRA
Urban Spring	TL	4/22/2011	0.23	122	19	23	4.4	LCRA
Urban Spring	TS	8/24/2010	0.87	130	24	50	2.6	LCRA
Urban Spring	TS	4/12/2011	0.91	146	28	64	2.5	LCRA
Urban Spring	TT	8/28/2010	1.7	105	22	40	2.2	LCRA
Urban Spring	TW	8/19/2010	0.2	146	32	30	1.8	LCRA
Urban Spring	TW	4/12/2011	0.18	138	33	30	1.6	LCRA
Urban Tributary	AE	7/24/2012	3.5	90	23	19	2.7	ICP-Q-MS (UT DGS)

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Site Type	Site Name	Collection Date	Sr (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Lab
Urban Tributary	AN	7/24/2012	2	97	21	74	4	ICP-Q-MS (UT DGS)
Urban Tributary	AS	7/24/2012	2.5	94	23	27	1.3	ICP-Q-MS (UT DGS)
Urban Tributary	CC	7/24/2012	0.77	130	26	59	3.4	ICP-Q-MS (UT DGS)
Urban Tributary	FB	3/7/2013	0.18	149	19	24	2.5	ICP-Q-MS (UT DGS)
Urban Tributary	FB	6/21/2013	0.17	151	18	22	1.7	ICP-Q-MS (UT DGS)
Urban Tributary	FE	7/24/2012	0.21	121	18	21	2.6	ICP-Q-MS (UT DGS)
Urban Tributary	FE	7/27/2012	0.2	116	17	20	2.5	ICP-Q-MS (UT DGS)
Urban Tributary	FE	8/10/2012	0.21	113	18	24	2.5	ICP-Q-MS (UT DGS)
Urban Tributary	FE	9/25/2012	0.2	114	17	22	2.5	ICP-Q-MS (UT DGS)
Urban Tributary	FE	3/7/2013	0.2	115	19	23	2.4	ICP-Q-MS (UT DGS)
Urban Tributary	FE	6/21/2013	0.17	94	16	16	2.3	ICP-Q-MS (UT DGS)
Urban Tributary	FG	3/7/2013	0.61	81	26	23	2.7	ICP-Q-MS (UT DGS)
Urban Tributary	FG	6/21/2013	0.46	75	21	18	2.6	ICP-Q-MS (UT DGS)
Urban Tributary	FN	7/24/2012	0.18	92	20	26	3.2	ICP-Q-MS (UT DGS)

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Site Type	Site Name	Collection Date	Sr (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Lab
Urban Tributary	FN	7/27/2012	0.18	87	20	26	3.1	ICP-Q-MS (UT DGS)
Urban Tributary	FN	8/10/2012	0.16	81	19	28	3.4	ICP-Q-MS (UT DGS)
Urban Tributary	FN	8/23/2012	0.16	85	18	26	3.2	ICP-Q-MS (UT DGS)
Urban Tributary	FN	9/25/2012	0.15	74	18	27	3.3	ICP-Q-MS (UT DGS)
Urban Tributary	FN	3/7/2013	0.13	67	19	29	3.1	ICP-Q-MS (UT DGS)
Urban Tributary	FN	6/21/2013	0.15	76	17	23	3.4	ICP-Q-MS (UT DGS)
Urban Tributary	FW	7/24/2012	0.27	125	24	31	3.1	ICP-Q-MS (UT DGS)
Urban Tributary	MV	7/24/2012	0.74	98	19	29	3.4	ICP-Q-MS (UT DGS)
Urban Tributary	PC	6/21/2013	0.89	110	22	43	1.9	ICP-Q-MS (UT DGS)
Urban Tributary	TR	7/24/2012	0.79	130	21	27	1.9	ICP-Q-MS (UT DGS)

Table S2.2 Municipal (supply and waste) water, and stream and spring water anion concentrations. * Indicates F analyses

Site Type	Site Name	Collection Date	SO_4 (ppm)	Cl (ppm)	HCO_3 (ppm)	NO_3 (ppm)	Lab	*F (ppm)	*Lab
Municipal Waste Water	CoA WWTP	6/14/2013	44	63	94	0.2	HPLC (UT DGS)	0.7	LaF_3 (UT DGS)
Municipal Waste Water	CoA WWTP	6/15/2013	49	70	166	0.3	HPLC (UT DGS)	0.6	LaF_3 (UT DGS)
Municipal Waste Water	CoA WWTP	6/17/2013	67	73	149	0.3	HPLC (UT DGS)	0.73	LaF_3 (UT DGS)
Municipal Waste Water	CoA WWTP	6/18/2013	38	81	165	0	HPLC (UT DGS)	0.41	LaF_3 (UT DGS)
Municipal Waste Water	CoA WWTP	6/20/2013	50	79	141	0	HPLC (UT DGS)	0.51	LaF_3 (UT DGS)
Municipal Waste Water	CoA WWTP	6/21/2013	52	57	113	0.2	HPLC (UT DGS)	0.55	LaF_3 (UT DGS)
Municipal Waste Water	CoA WWTP	6/22/2013	32	167	130	0.1	HPLC (UT DGS)	0.46	LaF_3 (UT DGS)
Municipal Waste Water	CoA WWTP	4/30/2011	41	63	156	0.4	LCRA	0.98	LCRA
Municipal Waste Water	CoA WWTP	5/1/2011	120	68	135	2.1	LCRA	1.19	LCRA
Municipal Supply Water	SBK	7/25/2012	32	43	60	0.8	HPLC (UT DGS)	0.72	LaF_3 (UT DGS)

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Site Type	Site Name	Collection Date	SO_4 (ppm)	Cl (ppm)	HCO_3 (ppm)	NO_3 (ppm)	Lab	*F (ppm)	*Lab
Municipal Supply Water	SBK	7/27/2012	30	44	60	2	HPLC (UT DGS)	0.66	LaF_3 (UT DGS)
Municipal Supply Water	SBK	8/10/2012	30	41	64	0.5	HPLC (UT DGS)	0.56	LaF_3 (UT DGS)
Municipal Supply Water	SBK	9/25/2012	29	43	76	0.8	HPLC (UT DGS)	0.67	LaF_3 (UT DGS)
Municipal Supply Water	CLB	6/21/2013	31	43	66	BDL	HPLC (UT DGS)	0.6	LaF_3 (UT DGS)
Municipal Supply Water	TCB	8/28/2010	22	27	68	1.1	LCRA	0.79	LCRA
Municipal Supply Water	TCB	4/15/2011	28	30	74	0.6	LCRA	0.6	LCRA
Rural Spring	FK	8/23/2010	15	16	344	0	LCRA	0.12	LCRA
Rural Spring	LN	8/24/2010	17	17	339	0	LCRA	0.11	LCRA
Rural Spring	LR	8/28/2010	15	16	356	0.8	LCRA	0.14	LCRA
Rural Spring	LR	4/12/2011	17	19	353	1.8	LCRA	0.13	LCRA
Rural Spring	LN	4/12/2011	21	20	339	0	LCRA	0.1	LCRA
Rural Spring	FK	4/12/2011	18	17	321	0	LCRA	0.1	LCRA
Rural Tributary	EN	7/24/2012	25	18	312	BDL	HPLC (UT DGS)	0.18	LaF_3 (UT DGS)
Rural Tributary	EM	7/24/2012	19	18	347	2.4	HPLC (UT DGS)	0.18	LaF_3 (UT DGS)

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Site Type	Site Name	Collection Date	SO_4 (ppm)	Cl (ppm)	HCO_3 (ppm)	NO_3 (ppm)	Lab	*F (ppm)	*Lab
Rural Tributary	ED	7/24/2012	32	24	353	2.5	HPLC (UT DGS)	0.19	LaF_3 (UT DGS)
Rural Tributary	EM	7/27/2012	20	19	359	1.7	HPLC (UT DGS)	0.19	LaF_3 (UT DGS)
Rural Tributary	ED	7/27/2012	31	26	336	3.5	HPLC (UT DGS)	0.21	LaF_3 (UT DGS)
Rural Tributary	EN	7/27/2012	27	19	308	0.8	HPLC (UT DGS)	0.17	LaF_3 (UT DGS)
Rural Tributary	PN	3/7/2013	18	16	312	BDL	HPLC (UT DGS)	0.1	LaF_3 (UT DGS)
Rural Tributary	PN	6/21/2013	18	17	322	BDL	HPLC (UT DGS)	0.09	LaF_3 (UT DGS)
Urban Spring	TW	8/19/2010	59	61	468	12.1	LCRA	0.27	LCRA
Urban Spring	SH	8/24/2010	71	88	407	28.7	LCRA	0.16	LCRA
Urban Spring	TF	8/24/2010	23	37	348	2	LCRA	0.1	LCRA
Urban Spring	TS	8/24/2010	79	76	398	1.6	LCRA	0.13	LCRA
Urban Spring	TL	8/28/2010	37	37	405	5.2	LCRA	0.32	LCRA
Urban Spring	TT	8/28/2010	62	58	299	0.3	LCRA	0.2	LCRA
Urban Spring	FY	8/29/2010	17	19	354	7.5	LCRA	0.08	LCRA
Urban Spring	BW	8/29/2010	61	65	364	5.1	LCRA	0.15	LCRA
Urban Spring	TB	8/29/2010	27	30	481	11	LCRA	0.14	LCRA
Urban Spring	TW	4/12/2011	54	56	428	7.6	LCRA	0.24	LCRA

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Site Type	Site Name	Collection Date	SO_4 (ppm)	Cl (ppm)	HCO_3 (ppm)	NO_3 (ppm)	Lab	*F (ppm)	*Lab
Urban Spring	SH	4/12/2011	71	83	399	28.7	LCRA	0.12	LCRA
Urban Spring	BW	4/12/2011	67	72	360	7.7	LCRA	0.13	LCRA
Urban Spring	TF	4/12/2011	20	29	373	1.8	LCRA	0.09	LCRA
Urban Spring	TB	4/12/2011	30	35	456	9.3	LCRA	0.14	LCRA
Urban Spring	TS	4/12/2011	105	92	368	2.2	LCRA	0.12	LCRA
Urban Spring	FY	4/15/2011	18	23	325	6.6	LCRA	0.09	LCRA
Urban Spring	TL	4/22/2011	42	43	344	7	LCRA	0.36	LCRA
Urban Tributary	FW	7/24/2012	59	62	376	9.7	HPLC (UT DGS)	0.31	LaF_3 (UT DGS)
Urban Tributary	FE	7/24/2012	47	42	358	4.5	HPLC (UT DGS)	0.33	LaF_3 (UT DGS)
Urban Tributary	FN	7/24/2012	44	54	295	4	HPLC (UT DGS)	0.42	LaF_3 (UT DGS)
Urban Tributary	TR	7/24/2012	55	57	377	16.6	HPLC (UT DGS)	0.19	LaF_3 (UT DGS)
Urban Tributary	AS	7/24/2012	54	62	286	8.3	HPLC (UT DGS)	0.22	LaF_3 (UT DGS)
Urban Tributary	AE	7/24/2012	86	41	250	BDL	HPLC (UT DGS)	0.24	LaF_3 (UT DGS)
Urban Tributary	CC	7/24/2012	103	91	376	6.9	HPLC (UT DGS)	0.19	LaF_3 (UT DGS)

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Site Type	Site Name	Collection Date	SO_4 (ppm)	Cl (ppm)	HCO_3 (ppm)	NO_3 (ppm)	Lab	*F (ppm)	*Lab
Urban Tributary	AN	7/24/2012	128	93	270	2.8	HPLC (UT DGS)	0.27	LaF_3 (UT DGS)
Urban Tributary	MV	7/24/2012	43	48	311	5.8	HPLC (UT DGS)	0.24	LaF_3 (UT DGS)
Urban Tributary	FE	7/27/2012	46	43	343	3.9	HPLC (UT DGS)	0.29	LaF_3 (UT DGS)
Urban Tributary	FN	7/27/2012	42	52	277	2.2	HPLC (UT DGS)	0.46	LaF_3 (UT DGS)
Urban Tributary	FE	8/10/2012	45	47	321	2.4	HPLC (UT DGS)	0.23	LaF_3 (UT DGS)
Urban Tributary	FN	8/10/2012	37	47	281	0.8	HPLC (UT DGS)	0.44	LaF_3 (UT DGS)
Urban Tributary	FN	8/23/2012	33	42	274	1.1	HPLC (UT DGS)	0.38	LaF_3 (UT DGS)
Urban Tributary	FE	9/25/2012	43	37	335	1.3	HPLC (UT DGS)	0.23	LaF_3 (UT DGS)
Urban Tributary	FN	9/25/2012	32	43	245	BDL	HPLC (UT DGS)	0.45	LaF_3 (UT DGS)
Urban Tributary	FE	3/7/2013	42	42	326	1.9	HPLC (UT DGS)	0.22	LaF_3 (UT DGS)

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Site Type	Site Name	Collection Date	SO_4 (ppm)	Cl (ppm)	HCO_3 (ppm)	NO_3 (ppm)	Lab	*F (ppm)	*Lab
Urban Tributary	FB	3/7/2013	43	38	443	13	HPLC (UT DGS)	0.22	LaF_3 (UT DGS)
Urban Tributary	FN	3/7/2013	38	47	258	BDL	HPLC (UT DGS)	0.45	LaF_3 (UT DGS)
Urban Tributary	FG	3/7/2013	51	40	285	BDL	HPLC (UT DGS)	0.23	LaF_3 (UT DGS)
Urban Tributary	FE	6/21/2013	31	28	328	BDL	HPLC (UT DGS)	0.22	LaF_3 (UT DGS)
Urban Tributary	FB	6/21/2013	44	36	448	12.6	HPLC (UT DGS)	0.21	LaF_3 (UT DGS)
Urban Tributary	FN	6/21/2013	29	39	264	BDL	HPLC (UT DGS)	0.39	LaF_3 (UT DGS)
Urban Tributary	PC	6/21/2013	70	60	333	BDL	HPLC (UT DGS)	0.11	LaF_3 (UT DGS)
Urban Tributary	FG	6/21/2013	27	28	281	BDL	HPLC (UT DGS)	0.22	LaF_3 (UT DGS)

Table S2.3 Municipal (supply and waste) water, and stream water, spring water, soil, and bedrock 87Sr/86Sr values with 2σ uncertainties.

Site Type	Site Name	Collection Date	$^{87}Sr/^{86}Sr$	2σ	Lab
Municipal Supply Water	TCB	8/28/10	0.709096	0.000005	TIMS (UT DGS)
Municipal Supply Water	SBK	7/25/12	0.709190	0.000006	TIMS (UT DGS)
Municipal Supply Water	SBK	7/27/12	0.709230	0.000006	TIMS (UT DGS)
Municipal Supply Water	SBK	8/10/12	0.709230	0.000006	TIMS (UT DGS)
Municipal Supply Water	TCB	4/15/11	0.709340	0.000006	TIMS (UT DGS)
Municipal Supply Water	CLB	6/21/13	0.709417	0.000006	TIMS (UT DGS)
Municipal Supply Water	SBK	9/25/12	0.709522	0.000006	TIMS (UT DGS)
Municipal Waste Water	CoA WWTP	6/15/13	0.707938	0.000008	TIMS (UT DGS)
Municipal Waste Water	CoA WWTP	6/20/13	0.708138	0.000008	TIMS (UT DGS)
Municipal Waste Water	CoA WWTP	5/1/11	0.708467	0.000008	TIMS (UT DGS)
Municipal Waste Water	CoA WWTP	6/21/13	0.708690	0.000002	TIMS (UT DGS)
Municipal Waste Water	CoA WWTP	4/30/11	0.708757	0.000006	TIMS (UT DGS)
Municipal Waste Water	CoA WWTP	6/22/13	0.708770	0.000002	TIMS (UT DGS)

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Site Type	Site Name	Collection Date	$^{87}Sr/^{86}Sr$	2σ	Lab
Municipal Waste Water	CoA WWTP	6/18/13	0.708840	0.000008	TIMS (UT DGS)
Municipal Waste Water	CoA WWTP	6/14/13	0.708984	0.000008	TIMS (UT DGS)
Municipal Waste Water	CoA WWTP	6/17/13	0.708987	0.000008	TIMS (UT DGS)
Urban Spring	FY	8/29/10	0.708154	0.000005	TIMS (UT DGS)
Urban Spring	FY	4/15/11	0.708175	0.000006	TIMS (UT DGS)
Urban Spring	TL	8/28/10	0.708202	0.000006	TIMS (UT DGS)
Urban Spring	TL	4/22/11	0.708223	0.000006	TIMS (UT DGS)
Urban Spring	TW	8/19/10	0.708557	0.000006	TIMS (UT DGS)
Urban Spring	TW	4/12/11	0.708578	0.000008	TIMS (UT DGS)
Urban Spring	SH	4/12/11	0.708746	0.000005	TIMS (UT DGS)
Urban Spring	SH	8/24/10	0.708748	0.000006	TIMS (UT DGS)
Urban Tributary	FW	7/24/12	0.708192	0.000005	TIMS (UT DGS)
Urban Tributary	FE	3/7/13	0.708207	0.000006	TIMS (UT DGS)
Urban Tributary	FE	9/25/12	0.708259	0.000006	TIMS (UT DGS)
Urban Tributary	FE	6/21/13	0.708270	0.000007	TIMS (UT DGS)

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Site Type	Site Name	Collection Date	$^{87}Sr/^{86}Sr$	2σ	Lab
Urban Tributary	FE	7/24/12	0.708282	0.000006	TIMS (UT DGS)
Urban Tributary	FE	8/10/12	0.708285	0.000006	TIMS (UT DGS)
Urban Tributary	FE	7/27/12	0.708286	0.000006	TIMS (UT DGS)
Urban Tributary	FB	3/7/13	0.708356	0.000006	TIMS (UT DGS)
Urban Tributary	FB	6/21/13	0.708393	0.000006	TIMS (UT DGS)
Urban Tributary	FN	9/25/12	0.708484	0.000006	TIMS (UT DGS)
Urban Tributary	FN	7/24/12	0.708494	0.000006	TIMS (UT DGS)
Urban Tributary	FN	7/27/12	0.708494	0.000006	TIMS (UT DGS)
Urban Tributary	FN	8/10/12	0.708518	0.000006	TIMS (UT DGS)
Urban Tributary	FN	6/21/13	0.708524	0.000008	TIMS (UT DGS)
Urban Tributary	FN	8/23/12	0.708530	0.000006	TIMS (UT DGS)
Urban Tributary	FN	3/7/13	0.708534	0.000006	TIMS (UT DGS)
Urban Spring	BW	8/29/10	0.707689	0.000005	TIMS (UT DGS)
Urban Spring	BW	4/12/11	0.707726	0.000006	TIMS (UT DGS)
Urban Spring	TF	8/24/10	0.707778	0.000006	TIMS (UT DGS)

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Site Type	Site Name	Collection Date	$^{87}Sr/^{86}Sr$	2σ	Lab
Urban Spring	TF	4/12/11	0.707789	0.000008	TIMS (UT DGS)
Urban Spring	TB	4/12/11	0.707854	0.00001	TIMS (UT DGS)
Urban Spring	TB	8/29/10	0.707873	0.000006	TIMS (UT DGS)
Urban Spring	TT	8/28/10	0.707932	0.000006	TIMS (UT DGS)
Urban Spring	TS	8/24/10	0.707992	0.000006	TIMS (UT DGS)
Urban Spring	TS	4/12/11	0.708047	0.00001	TIMS (UT DGS)
Urban Tributary	TR	7/24/12	0.707792	0.000005	TIMS (UT DGS)
Urban Tributary	FG	3/7/13	0.707820	0.000006	TIMS (UT DGS)
Urban Tributary	PC	6/21/13	0.707852	0.000006	TIMS (UT DGS)
Urban Tributary	AS	7/24/12	0.707857	0.000006	TIMS (UT DGS)
Urban Tributary	FG	6/21/13	0.707920	0.000006	TIMS (UT DGS)
Urban Tributary	AE	7/24/12	0.707931	0.000006	TIMS (UT DGS)
Urban Tributary	CC	7/24/12	0.708152	0.000006	TIMS (UT DGS)
Urban Tributary	AN	7/24/12	0.708180	0.000006	TIMS (UT DGS)
Urban Tributary	MV	7/24/12	0.708229	0.000006	TIMS (UT DGS)

Site Type	Site Name	Collection Date	$^{87}Sr/^{86}Sr$	2σ	Lab
Rural Spring	LR	4/12/11	0.708084	0.000008	TIMS (UT DGS)
Rural Spring	LR	8/28/10	0.708045	0.000006	TIMS (UT DGS)
Rural Spring	LN	4/12/11	0.707971	0.000008	TIMS (UT DGS)
Rural Tributary	PN	6/21/13	0.707965	0.000006	TIMS (UT DGS)
Rural Spring	LN	8/24/10	0.707934	0.000005	TIMS (UT DGS)
Rural Spring	FK	8/23/10	0.707871	0.000006	TIMS (UT DGS)
Rural Spring	FK	4/12/11	0.707856	0.000008	TIMS (UT DGS)
Rural Tributary	EM	7/27/12	0.707819	0.000005	TIMS (UT DGS)
Rural Tributary	EN	7/24/12	0.707814	0.000006	TIMS (UT DGS)
Rural Tributary	ED	7/27/12	0.707813	0.000005	TIMS (UT DGS)
Rural Tributary	EM	7/24/12	0.707812	0.000006	TIMS (UT DGS)
Rural Tributary	ED	7/24/12	0.707808	0.000005	TIMS (UT DGS)
Rural Tributary	EN	7/27/12	0.707806	0.000006	TIMS (UT DGS)
Rural Tributary	PN	3/7/13	0.707798	0.000006	TIMS (UT DGS)
Brackett, Unirrigated Soil	LPS1	n/a	0.708002	0.000006	TIMS (UT DGS)

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Site Type	Site Name	Collection Date	$^{87}Sr/^{86}Sr$	2σ	Lab
Brackett, Unirrigated Soil	LPS2	n/a	0.707920	0.000006	TIMS (UT DGS)
Tarrant, Unirrigated Soil	LPS3	n/a	0.708185	0.000006	TIMS (UT DGS)
Tarrant, Unirrigated Soil	LPS4	n/a	0.708049	0.000006	TIMS (UT DGS)
Tarrant, Unirrigated Soil	LPS5	n/a	0.708235	0.000006	TIMS (UT DGS)
Tarrant, Unirrigated Soil	SES1	n/a	0.707851	0.000006	TIMS (UT DGS)
Tarrant, Unirrigated Soil	SES1-W	n/a	0.707847	0.000006	TIMS (UT DGS)
Volente, Unirrigated Soil	SES2	n/a	0.708069	0.000006	TIMS (UT DGS)
Volente, Unirrigated Soil	TRS1	n/a	0.708073	0.000006	TIMS (UT DGS)
Brackett, Unirrigated Soil	TWB	n/a	0.708030	0.000006	TIMS (UT DGS)
Tarrant, Unirrigated Soil	TWT	n/a	0.708353	0.000006	TIMS (UT DGS)
Tarrant, Irrigated Soil	WFH	n/a	0.708701	0.000006	TIMS (UT DGS)
Tarrant, Irrigated Soil	XB	n/a	0.709134	0.000018	TIMS (UT DGS)
Tarrant, Irrigated Soil	XS	n/a	0.708873	0.000006	TIMS (UT DGS)
Tarrant, Irrigated Soil	10007 CLL	n/a	0.708919	0.000005	TIMS (UT DGS)
Tarrant, Irrigated Soil	10007 CLU	n/a	0.708948	0.000006	TIMS (UT DGS)

Site Type	Site Name	Collection Date	$^{87}Sr/^{86}Sr$	2σ	Lab
Brackett, Irrigated Soil	11038 GC	n/a	0.709010	0.000006	TIMS (UT DGS)
Brackett, Unirrigated Soil	360-s-1-2016	n/a	0.708014	0.000006	TIMS (UT DGS)
Brackett, Irrigated Soil	360-s-4-2016	n/a	0.708519	0.000006	TIMS (UT DGS)
Brackett, Irrigated Soil	360-s-4-2016 DI	n/a	0.708978	0.000007	TIMS (UT DGS)
Brackett, Irrigated Soil	360-s-5-2016	n/a	0.709058	0.000006	TIMS (UT DGS)
Volente, Irrigated Soil	4005 SSL	n/a	0.708867	0.000006	TIMS (UT DGS)
Volente, Irrigated Soil	4005 SSU	n/a	0.708807	0.000007	TIMS (UT DGS)
Brackett, Unirrigated Soil	5002 LCB	n/a	0.707902	0.000006	TIMS (UT DGS)
Brackett, Irrigated Soil	5002 LCF	n/a	0.708668	0.000006	TIMS (UT DGS)
Tarrant, Irrigated Soil	9613 TBL	n/a	0.708764	0.000006	TIMS (UT DGS)
Tarrant, Irrigated Soil	9613 TBU	n/a	0.708746	0.000006	TIMS (UT DGS)
Tarrant, Unirrigated Soil	CU-1	n/a	0.708408	0.000005	TIMS (UT DGS)
Edwards Formation, Bedrock	FP1	n/a	0.707623	0.000006	TIMS (UT DGS)
Walnut Formation, Bedrock	FP2	n/a	0.707674	0.000006	TIMS (UT DGS)

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Site Type	Site Name	Collection Date	$^{87}Sr/^{86}Sr$	2σ	Lab
Glen Rose Formation, Bedrock	FP3	n/a	0.707597	0.000006	TIMS (UT DGS)
Comanche Peak Formation, Bedrock	FP4	n/a	0.707666	0.000006	TIMS (UT DGS)
Walnut Formation, Bedrock	GHT1	n/a	0.707604	0.000006	TIMS (UT DGS)
Edwards Formation, Bedrock	GHT2	n/a	0.707646	0.000005	TIMS (UT DGS)
Edwards Formation, Bedrock	GHT2-NPT	n/a	0.707685	0.000006	TIMS (UT DGS)
Edwards Formation, Bedrock	GHT3	n/a	0.707625	0.000007	TIMS (UT DGS)
Glen Rose Formation, Bedrock	SE1	n/a	0.707817	0.000007	TIMS (UT DGS)
Glen Rose Formation, Bedrock	SE2	n/a	0.707769	0.000005	TIMS (UT DGS)
Glen Rose Formation, Bedrock	SE2-WR	n/a	0.707747	0.000005	TIMS (UT DGS)

Table S2.4 Cation Replicates

Site Classification	Site Name	Collection Date	Sr (ppm)	Ca (ppm)	Mg (ppm)	Na (ppm)	K (ppm)	Lab
Urban Tributary	FN	8/10/12	0.16	81.5	18.3	27.6	3.3	ICP-Q-MS (UT DGS)
Urban Tributary	FE	8/23/12	0.20	113	17.6	20.6	2.5	ICP-Q-MS (UT DGS)
Urban Tributary	FE	8/23/12	0.20	111	17.9	21.0	2.5	ICP-Q-MS (UT DGS)
Urban Tributary	FB	3/7/13	0.18	151	18.5	23.6	2.5	ICP-Q-MS (UT DGS)
Urban Tributary	PC	6/21/13	0.75	111	21.4	42.8	1.9	ICP-Q-MS (UT DGS)

Table S2.5 Anion Replicates

Site Classification	Site Name	Collection Date	Cl (ppm)	SO_4 (ppm)	NO_3 (ppm)	Lab	*F (ppm)	*Lab
Urban Tributary	FN	8/10/12	46.4	36.6	0.6	HPLC (UT DGS)	0.25	LaF_3 (UT DGS)
Urban Tributary	FE	8/23/12	34.3	40.3	1.2	HPLC (UT DGS)	0.24	LaF_3 (UT DGS)
Urban Tributary	FB	9/25/12	33.1	32.0	3.8	HPLC (UT DGS)	0.21	LaF_3 (UT DGS)
Urban Tributary	FB	3/7/13	39.0	43.5	13.8	HPLC (UT DGS)	0.23	LaF_3 (UT DGS)
Rural Tributary	PN	6/21/13	16.8	17.9	BDL	HPLC (UT DGS)	0.38	LaF_3 (UT DGS)

Table S2.6 Field blank analyses. TIMS analyses is in pg, and ICP-MS, HPLC, and ISE analyses is in ppm. BDL indicates measurements below detection limit.

	TIMS	ICP-MS					HPLC			ISE
Collection Date	**Sr (pg)**	**Sr**	**Ca**	**Mg**	**Na**	**K**	**Cl**	**SO_4**	**NO_3**	**F**
7/24/12	16	BDL	BDL	BDL	BDL	BDL	3.7	BDL	1.1	BDL
7/27/12	138	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.9	BDL
8/10/12	121	BDL	0.35	BDL	0.16	0.13	BDL	BDL	BDL	BDL
8/23/12	21	BDL	0.33	BDL	0.09	0.07	BDL	BDL	BDL	BDL
9/25/12	22	BDL	0.08	BDL	BDL	0.03	BDL	BDL	BDL	BDL
3/7/13	5529	0.004	4.8	0.05	BDL	BDL	0.5	BDL	BDL	BDL
6/21/13	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL